#3269

X-10
Mercury

3-12-96
SMF

Memorandum GO-144

To K|X search for Hg documents 19

From K-1004 labs

Subject: K-1024 ES

~~166 envir. data~~ K-1401 VPS

~~226 ORR envir. data~~ K-1420 MRecovery

~~227 "~~ K-1037?

~~234 K envir data~~ K-29

~~254 ORR envir data~~

~~373 "~~

~~374 "~~

~~1059 '91 remed. plan~~

~~1242 '86 ORR~~

~~1309 Walker Branch~~

~~1314 Gordon's W.Bar bluegill~~

✓1014 Lloyd|Gore

HAVE 1130 K ~~hist.~~ release ~~est.~~ '85

~~✓1135 K electronics shop~~ (68? 70)

~~1190 K PIOs 1983~~

~~1194~~ R (K1024) elec. shop

• 1385 '63 K HP in Hg (bldgs?)

?✓1386 '46-63 K air data

~~✓1403 EATC~~ Holston River (Hg) W. Branch (Hg)

• 1441 YM 59-72 Hg releases K

• 1443 YM 46-49 Hg releases (vacuum pump shop K-1401)

• 1571 (~~'46-60?~~ ~~BL~~ | K1024) air

?(1602 '54 U reduction X

• 1631 invu: S. Breeder

• 1629 invu: John Chandler X-LOOREX

• 1526 invu: Rbt. Schaich X-10 gwrd

1525 invu: Rbt. Brookbank X-10

~~485 K monthlies~~

~~738 TSCA invu.~~

✓779 K|X FOI

✓783 9/55 K H_2O monthlies

• 784 7/55 K H_2O study

• 786 (12-47 > K-1401, K-1004A; 5-48 47-48 (4)) K air Hg 2 IH appendices to HP reports

✓804 '46 K air Hg

• 806 5-48 7-48 48 K (Depts (rooms | locations?))

• 807 '47 (3) K (fish?) (IH report) (K-1004 K-1401)

• 809 '46 K analytical

• 810 (See 2111) '46 K purifying Hg

• 811 '48 K inventory

• 812 K Hg air

• 821 '48 K HP rpt.

• 822 '49 K Hg use

• 827 '46 Hg purification

• 837 '54 K Hg cathode

B 858 invu: Dykstra

B 859 invu: Keller

B 1203 invu: Legacy

~~1499 invu: Bevelheimer~~ (envir. BI)

• 1516 invu: Bill Burch Hg X-10 (1000 gals?)

✓1668 invu: Wilcox

~~1677 mmHg~~

~~1769 PCBs WOC~~

• 1849 '54-62 Hg air | K1004L

• 1868 '48 IH air Hg (K-1004 + Fenelon)

• 1872 '48 K Chem Ops reports: Hg recovery

✓1900 '46 Summ. Report of the Fenelon (K-25, K-27, ↓)

• 1983 YM Hg in fuel reg. X (see abstract)

SMF moved to Nile • 2003 '63 Hg in colanolin Hanford 1965 (acid) waste EIW Soln. prior to EU } solvent extraction of fixation

• 2032 invu: Stan A. X

2033 invu: Bill Unger Hg zg & dissolution catalyst

~~2035 invu: Weinberg~~ canot. tol. plants Hg

~~2083 '87 ORR envir~~

• 2104 '60-63 Hg air | K1420 Hg Recovery Room

• 2107 47-49 IH's committee K

• 2111 ? distill Hg Hg K (Nolite mtg)

~~1849 Hg IH air K~~ (bldgs?)

~~2126 '46 analytical K~~

2145 '47 trip to Rock K

• 2203 '54 valve? bellows? Hg (K-29)

~~2210 '47 trip to Roch. (bldgs?)~~

~~✓2226 Phelps Dodge~~

~~2263 >60's K770 scrapyard PCBs~~

~~2265 Hg in instruments K707 switchhouse PCBs~~

• 2370 '49-51 K-25 Hg labs IH surveys - Hg Recovery Unit

When requested, send original and one copy.

X/K Hg Documents 3/12/96 SMF

No Folder
(? Missing) / Empty Folder

Repo No.

810 - possibly never got a copy b/c doesn't say a copy was retrieved JKL 2-93

811 - no copy JKL 2-93 — looks like Ni - you probably have these out!

812?? "

821 - no copy "

822 prob no copy.

827 prob no copy

837 no copy "

1385 - no copy?? " 4-95

1386 box - no copy ↓

1441	UYM 5-95	COPYLOC = STO
1602	UYM 6-95	"
1872	JKL 7-95	- at Shonka's
2125 (ka 1849)	JKL 11-95	- no copy?? → no copy location given

Do I ask Sylvia to send these? What's the protocol? ask Shonka

TITLE/1 Process Division Process Design and Development Department
Purification of Contaminated Mercury
DOCNBR/1 3.108.1 never retrieved
AUTHORS/1 J. George
PUBLDAT/1 08/19/46
CLSSCAT/1 A
STADDR/1 K
SOURCE/1 K-25 ATL
CATPRIM/1 hs
ENTERED/1 02/09/93
REPNBR/1 810
ENTRBY/1 cmv
KYWRDS/1 Mercury
KYWRDS/2 Distillation
KYWRDS/3 Recovery
KYWRDS/4 Waste recovery
KYWRDS/5 Purification
ABSTRCT/1 Describes a procedure for purifying contaminated mercury. No explanation as to why the mercury needs purifying. A drawing of the mercury washer and a drawing of the mercury refining still are included.
REVIEWR/1 J. Lamb
REVDATE/1 01/27/93
$
TITLE/1 Process Division Chemical Operations Department Annual Report 1947
DOCNBR/1 K - 138 never retrieved
AUTHORS/1 Hartman, W. C.
PUBLDAT/1 02/17/48
CLSSCAT/1 A
STADDR/1 K
SOURCE/1 K-25 ATL
CATPRIM/1 hp
ENTERED/1 02/09/93
REPNBR/1 811
ENTRBY/1 cmv
KYWRDS/1 Production
KYWRDS/2 Decontamination
KYWRDS/3 Uranium recovery
KYWRDS/4 Mercury
KYWRDS/5 Fluoride
ABSTRCT/1 This is the first annual report of the chemical Operation Department. The report describes production, major developments and services for 1947. It includes information on the quantities of various chemicals used and produced on the plant. Chemicals reported are fluorine, nitrogen, uranium hexafluoride, uranium recovery, freon recovery, oil recovery, mercury recovery.
REVIEWR/1 J. Lamb
REVDATE/1 01/27/93
$
TITLE/1 Combined Report of Chemical Urinary Findings and Industrial Hygiene Field Investigations for Fourth Quarter, 1948
DOCNBR/1 K - 247, Part 4 never retrieved
AUTHORS/1 W. H. Baumann
PUBLDAT/1 02/11/49
CLSSCAT/1 A
STADDR/1 K
SOURCE/1 K-25 ATL
CATPRIM/1 sa
ENTERED/1 02/09/93
REPNBR/1 812
ENTRBY/1 cmv
KYWRDS/1 Room air samplnig
KYWRDS/2 Urinalysis
KYWRDS/3 Room air monitoring
ABSTRCT/1 This report is a compilation of results of chemical urinary findings and environmental non-radiation findings for the fourth quarter of

1948. Chemical urinary findings are reported for plutonium, uranium, fluorides, mercury, and beryllium. Room air non-radiation findings are reported for mercury, fluoride, nickel, uranium, phosgene, nitrogen oxides, trifluorochloroethylene (Monomer), carbon tetrachloride, trichloroethylene.
. /IEWR/1 J. Lamb
REVDATE/1 01/27/93
$
TITLE/1 Report of Health Physics Activities for January - April, 1948 and June - November 1948
DOCNBR/1 K - 178 parts 1-4 and 6-11 never retrieved
AUTHORS/1 S. Visner
AUTHORS/2 C. L. Gritzner
PUBLDAT/1 00/00/48
CLSSCAT/1 A
STADDR/1 K
SOURCE/1 K-25 ATL
CATPRIM/1 HO
CATSEC/1 ew
CATSEC/2 sw
ENTERED/1 02/09/93
REPNBR/1 821
ENTRBY/1 cmv
KYWRDS/1 Health physics
KYWRDS/2 Surface water monitoring
KYWRDS/3 Waterborne effluents
KYWRDS/4 Industrial hygiene
KYWRDS/5 Mercury
KYWRDS/6 Trichloroethylene
KYWRDS/7 Beryllium
KYWRDS/8 Room air monitoring
KYWRDS/9 Personnel Monitoring
KYWRDS/10 Material releases
/RDS/11 Carbon tetrachloride
KYWRDS/12 Nickel
ABSTRCT/1 Health physics monthly progress reports. These reports include information on both effluent and environmental water monitoring data, material releases within buildings, room air sampling data for chemicals, personnel monitoring data, and room air monitoring data for radionuclides.
REVIEWR/1 J. Lamb
REVDATE/1 01/12/93
$
TITLE/1 Report of Meeting Between Barrier and Metallurgy Personnel and E. M. Wise on April 19, 1949
DOCNBR/1 KLI 236 never retrieved
AUTHORS/1 R. J. Elbert
PUBLDAT/1 05/20/49
CLSSCAT/1 A
STADDR/1 K
SOURCE/1 K-25 ATL
CATPRIM/1 hs
ENTERED/1 02/09/93
REPNBR/1 822
ENTRBY/1 cmv
KYWRDS/1 Mercury
KYWRDS/2 Silver
KYWRDS/3 Tin
KYWRDS/4 Nickel
ABSTRCT/1 This document summarizes a meeting between E. M. Wise and the Metallurgy Department personnel. The important points in this document regard the use of merucry, silver, and tin. Nickel is also refrenced in this document.
REVIEWR/1 J. Lamb
REVDATE/1 01/12/93
$

TITLE/1 Process Division, Process Design and Development Department Bi-Weekly Progress Report for Weeks Ending May 10, 1946 and July 5, 1946
DOCNBR/1 KZ-264 never retrieved
DOCNBR/2 KZ-238
AUTHORS/1 G. A. Garrett
RELDAT/1 00/00/46
CLSSCAT/1 A
STADDR/1 K
SOURCE/1 K-25 ATL
ENTERED/1 02/09/93
REPNBR/1 827
ENTRBY/1 cmv
KYWRDS/1 History
KYWRDS/2 Mercury
KYWRDS/3 Freon
KYWRDS/4 Compound T
KYWRDS/5 Compound X
KYWRDS/6 Chemical development
KYWRDS/7 Material balance
ABSTRCT/1 Reports on material balance, separation performance, chemical development, uranium recovery from solutions, mercury purification, freon recovery, and other process related studies.
REVIEWR/1 J. Lamb
REVDATE/1 01/26/93
$

TITLE/1 The Use of the High Current Mercury Cathode in Uranium Determination
DOCNBR/1 K - 1106 never retrieved
AUTHORS/1 J. Gurney
AUTHORS/2 T. W. Bartlett
AUTHORS/3 E. D. Marshall
AUTHORS/4 R. H. Lafferty
PUBLDAT/1 02/26/54
CLSSCAT/1 unc
STADDR/1 K
SOURCE/1 K-25 ATL
CATPRIM/1 hr
ENTERED/1 02/09/93
REPNBR/1 837
ENTRBY/1 cmv
KYWRDS/1 Research and development
KYWRDS/2 Analytical procedure
ABSTRCT/1 Electrolysis with mercury cathode operating at 20 amp was tested as a method for the rapid purification of uranium solutions prior to volumetric determination of the uranium. This high current mercury cathode was much faster than the conventional type of mercury cathode, and no further chemical purification is necessary prior to volumetric determination as is the case with solvent extraction.
REVIEWR/1 J. Lamb
REVDATE/1 02/26/93
$
TITLE/1 Environmental Conditions January - December 1963
DOCNBR/1 K - 1034A Box 8A - 3 - 34
AUTHORS/1 Safety, Health Physics, and Industrial Hygiene
PUBLDAT/1 1963
CLSSCAT/1 UNK
STADDR/1 K
SOURCE/1 K-25 Site Records
CATPRIM/1 hs
ENTERED/1 04/17/95 Box
REPNBR/1 1385
ENTRBY/1 SMG
KYWRDS/1 health physics
KYWRDS/2 industrial hygiene
KYWRDS/3 mercury
KYWRDS/4 hydrogen fluoride
KYWRDS/5 uranium
KYWRDS/6 air sample
KYWRDS/7 wipe sample
KYWRDS/8 personnel
ABSTRCT/1 These are the health physics and industrial hygiene contamination reports. They contain many surface or wipe samples, some air samples, and some personnel contamination results. There are also sampling data for mercury, hydrogen fluoride, isopropanol, and ammonia. The sampling records include all plant buildings for 1963.
REVIEWR/1 Lamb, J. K.
REVDATE/1 04/04/95
DTPSTART/1 01/01/63
DTPSTOP/1 12/31/63
$
TITLE/1 Industrial Hygiene, Field Sampling Reports
DOCNBR/1 K 1034A Box 12 - 2 - 27
AUTHORS/1 Duncan
PUBLDAT/1 1946-1963 Box
CLSSCAT/1 UNK
STADDR/1 K
SOURCE/1 K-25 Site Records
ENTERED/1 04/17/95
REPNBR/1 1386
ENTRBY/1 SMG
KYWRDS/1 industrial hygiene
KYWRDS/2 mercury

KYWRDS/3 uranium
KYWRDS/4 indoor air
KYWRDS/5 monitoring
ABSTRCT/1 This box contains industrial hygiene field sampling reports for buildings K-1024, K-1004L, and K-1420. The samples are indoor air samples for mercury and uranium.
REVIEWR/1 Lamb, J. K.
REVDATE/1 04/03/95
DTPSTART/1 1946
DTPSTOP/1 1963
$
TITLE/1 J-1004L Air Analyses Folder 1954-1962
AUTHORS/1 Stoddard, D. L.
PUBLDAT/1 1962
CLSSCAT/1 UNC
STADDR/1 K
SOURCE/1 Box 12-2-5-27
CATPRIM/1 sa
ENTERED/1 11/17/95
REPNBR/1 2125
ENTRBY/1 SMG
KYWRDS/1 air monitoring
KYWRDS/2 mercury
KYWRDS/3 fluorine
KYWRDS/4 chlorine trifluoride
KYWRDS/5 uranium
KYWRDS/6 K-1004L
ABSTRCT/1 Indoor air sample results for various chemical and radionuclide substances. The table gives the building or area location (in this case all samples were in the K-1004L laboratory), the date of the sample, the sampling time, the contaminant, the analytical result, and any observations or remarks. Chemical contaminants reported include: fluorine, chlorine trifluoride, mercury, uranium, lead, and hydrogen fluoride.
REVIEWR/1 Lamb, J. K.
REVDATE/1 08/10/95
DTPSTART/1 1954
DTPSTOP/1 1962
$

!? I'm not sure about this one
I may have a copy of this somewhere or a may not have retrieved it because it was in the air. It sounds very familiar though.. I think I may have sent it to someone.

Susan,

I looked over your list. The majority of the documents are documents that I did <u>not</u> <u>retrieve</u> (In Phase I the classification system was so backed up I wrote up a lot of OSF's to flag documents for Phase II but I did not request them.) Because all the documents have R-25 #'s it will be pretty easy to request them through R-25 (Sheila) if you want me to take care of it I will.

Two documents appear to be <u>boxes</u>

#1385 - (I wasn't actually writing up the box but these documents make up the majority of the box)
#1386
~~[illegible]~~ - Ask me about these.

Three documents are at Shonka's - just call Sylvia and ask her to track them down.

#1441
#1602
#1872

(Dupe of #1849) The last document ~~#2125~~ - does not say I ever retrieved a copy - but it sounds very familiar - I think I had or have a copy of it around here - I took a quick look and I could not find it. I may have sent it to someone before I had a document # for it and told them to watch out for any document #'s coming through InMagic - anyway - I'll check w/Jim if I can't locate it I'll snag another copy next time I'm out in OR.

~JKL

SRA
Shonka Research Associates, Inc.

June 21, 1996

To: S. Flack, Task 2

From: U. Young Moon

Re: CF Database keyword search at the X-10 Laboratory Records regarding missing documents for Task 2

Memo No. UYM.116

cc: T. Mongan (no attachments)
J. Shonka (no attachments)
T. Widner (no attachments)
SRA File

At the X-10 Laboratory Records (LR), the Central Files (CF) Database lists documents from 1942 through 1975. Although there are 79,000 document entries in the database, 19,000 of those documents are missing from the X-10 LR Vault. These missing documents were not reviewed because they are not available; however, if a document is of potential interest, an effort should be made to locate the document at other facilities, records centers, or from other individuals.

For Task 2, keywords listed below were used to search the database. The results of the keyword search are attached. Please review the attached list and note if any of the documents are of potential interest. I will attempt to locate documents you select at other facilities. If you have any questions, contact me.

Keywords:

Mercury, solvent, Hg, alloy, industrial hygiene, colex, elex, purex, orex, hermex, metallex, K-1024, K-1303, K-1420

4939 Lower Roswell Road, Suite 106
Marietta GA 30068
(770) 509-7606 ph.
(770) 509-7507 fax

Fileno (7)	Title	Auth 211 hits	To	In
CF-42-8-5	Question of Heat Conductivity of Tuballoy at High Temperatures	Smyth	Stearns	N
CF-43-1-30	Transmittal of Metal Tube and High Nickel Alloy	Brown	Priest	N
CF-43-10-359	Corrosion Rate of Tuballoy in Water Distilled at Various Temperatures	Draley		N
CF-43-11-373	Du Pont Tuballoy Outgassing Revere Mill Practice	Eqald		N
CF-43-2-138	Weekly Summary Report, Week Ending Feburary 25, 1943 - Solubility of Uranium Coating Alloys in Nitric Acid	Peterson, J.H.	Sutton, J.B.	N
CF-44-10-32	VOID - Rolling of Tuballoy	Howe	Memo	N
CF-44-10-577	Engr. Dev. System for Accounting for Tuballoy in Site B	Lyon	Foote	N
CF-44-11-46	Five Al/Si Die-Cast Bonded W-Slugs Made with A13 and A360 AL Alloys	Parker	Yancey	N
CF-44-11-662	Enriched Tuballoy	Turkevich	Borst	N
CF-44-12-469	The Slow Neutron Cross Section of Indium, Gold, Silver, Antimony, Lithium, and Mercury as Measured with a Neutron Beam Spectrometer	Havens		N
C 14-2-216	Interaction between Aluminum and Tuballoy	Howe	Cooper	N
CF-44-2-512	Hydrogen Analysis of 1.094" Dia. Plain Extruded Tuballoy Rod After Outgassing	Ewald	Hess	N
CF-44-2-513	Hydrogen Analysis of Machined Tuballoy Slug Samples Before and After Outgassing	Ewald	Hess	N
CF-44-2-514	Mill Practice Outgassing Tuballoy Rod	Ewald	Hess	N
CF-44-3-158	Cold Drawing of Tuballoy Rods at Joslyn Manufacturing and Supply Co., Fort Wayne, Indiana, February 23-26, 1944	Simmons	Grininger	N
CF-44-3-352	VOID - Designing of Production Units Cooled by Bismuth Alloy	Szilard	Compton	N
CF-44-6-692	Memo by Dr. Kamen Concerning Tuballoy Tracer	Jenkins	Whitaker	N
CF-44-8-562	Molybdenum-Uranium Alloys - Worked on at Ames and Y	Gurinsky	Allison	N
CF-44-8-643	Metallographic Polishing of Tuballoy for Grain Structures Determination P.A.	Parker		N
CF 45-1-448	Re: Irradiation of Tuballoy Foil and Request for 2 Slugs - Teletype NR-106	Bartky	Whitaker	N
CF-45-1-449	Request for Irradiation of Tuballoy Foil	Bartky	Chapman	N

Fileno	Title	Auth	To	In
CF-45-1-462	Request for Information Re: Br, Te, I, Au, Cu, Hg, Ag, and Pt Tracers	Lum	Doan	N
CF-45-1-475	Request for Irradiation of Tuballoy Carbide	Murphy	Doan	N
CF-45-1-526	Request for Irradiation of Tuballoy Carbide	Murphy	Whitaker	N
CF-45-1-678	Request for Irradiation of One G.M. of Tuballoy Foil	Bartky	Whitaker	N
CF-45-1-689	Information Pertaining to Depleted Tuballoy	Murphy	Doan	N
CF-45-1-695	Final Report Activity from Rare Tuballoy in Pile Water Sec. I-II			N
CF-45-10-270	Intra-Plant Transfer of 40 Tuballoy Disks - NRL-39	Coe	Briggs, R.B.	N
CF-45-10-271	Shipping Memo 194 for Tuballoy Disks	Bergantz	Coe	N
CF-45-10-393	Separation Processes Involving Alloy Formations	Voigt		N
CF-45-2-288	Reports on Electroplating of Tuballoy onto Other Metals and Harris Thesis on Polarography	Fussler	Fagerhaugh	N
CF-45-2-403	Request for Irradiation of Tuballoy Foil	Doan	Leverett	N
CF-45-2-419	Intra-Plant Transfer of Depleted Tuballoy	Doan	Johnson	N
CF-45-2-546	Request for Irradiation of Tuballoy Foils	Doan, R.L.	Leverett, M.C.	N
CF-45-3-135	Metallurgy of Uranium and Its Alloys	Warner		N
CF-45-3-136	Outline for Volume 12A - Metallurgical Project Record - Metallurgy of Uranium and Its Alloys	Warner		N
CF-45-3-410	Irradiation of Product in Tuballoy at Clinton	Jones	Furney	N
CF-45-3-417	Transmittal of Tuballoy Foil for Irradiation	Doan	Leverett	N
CF-45-3-418	Shipping Memo 80 for Tuballoy Foil	Murphy	Doan	N
CF-45-3-438	Transmittal Letter for PC of Two Excerpts from the Journal of Industrial Hygiene and Toxicology	Buettner	Stone	N
CF-45-4-319	Transfer of Tuballoy Trioxide - SoB-20	Murphy	Doan	N
CF-45-4-320	Shipping Memo No. 96 for Tuballoy Trioxide SoB-20	Murphy	Doan	N
CF-45-4-325	Transfer of Tuballoy Sample in the form of T(sub 3)O(sub 8)	Murphy	Doan	N
CF-45-5-352	Transmittal of Tuballoy Oxide	Murphy	Doan	
CF-45-5-353	Shipping Memo #113 for Tuballoy Oxide - TO(sub 2)	Murphy	Doan	N
CF-45-6-328	Corrosion of Fissionable Alloys	Brugmann	Allen	N

Fileno	Title	Auth	To	In
CF-45-6-378B	Irradiation of Ionium and Myrnalloy	Hay	Doan	N
CF-45-6-379B	Shipping Memo 123 for Myrnalloy Hydroxide	Hay	Doan	N
C 5-6-389	Irradiation of Product in Tuballoy	Hilberry	Whitaker	N
CF-45-6-390	Request for Irradiation of Product in Tuballoy	Jones	Whitaker	N
CF-45-6-487	Transfer of 21.7 Mg. of Product 49 Pure as Oxide in Tuballoy Slug #29	Doan	Stoughton	N
CF-45-8-347	Contract W-7405 eng-39 - Case No. S-2787 - Beta Emitter to Indicate the Penetration of Bonding Alloy into Aluminum Protective Can	Evans		N
CF-45-8-448	Intra-Plant Transfer of Myrnalloy	Doan	Steahly	N
CF-45-9-294	Intra-Plant Transfer of Myrnalloy	Doan	English	N
CF-45-9-298	Intra-Plant Transfer of Myrnalloy Disc	Doan	Jacobsen	N
CF-45-9-299	Shipping Memo #172 for One Myrnalloy Disc	Hay	Doan	N
CF-46-1-263	VOID - Re: Mercury vs. Steam Plants for Atomic Power	Young	Zinn	N
CF-46-1-488	Plans for Having Samples Exposed at Hanford in Order to Determine Effects of Irradiation on Alloys	Kyger	Bergantz	N
CF-46-10-337	Letter Describing the Etching Technique Used to Identify the Compounds in the Aluminum Alloys	Grenell		N
CF-46-10-406	Myrnalloy Report, Book 7			N
CF-46-10-84	Shipping Memorandum for Six Sheet Alclad Al-U Alloy	Grenell	Kyger	N
CF-46-11-341	Myrnalloy Report - Book 8			N
CF-46-11-343	Myrnalloy Report for October 1946	Whitlock	Lewis	N
CF-46-11-68	Myrnalloy and Myrnalloy Compounds Requirements	Murphy	McCullough	N
CF-46-12-25	VOID - Declassification of Report on Determination of Densities of Several Tuballoy Compounds	Miles	Batson	N
CF-46-12-254	Re: Irradiation of AL-235 Alloy in Pile	Greninger	Leverett	N
CF-46-12-410	Myrnalloy Report Book 9			N
CF-46-12-86	Shipping Memorandum for Alelod AL-Ta Alloys	Grenell	Kyger	N
C 46-2-269	Table of Samples of Alclad in Alloy	Grenell	Kyger	N
CF-46-2-381	Plans for Testing Properties of Irradiated Alloys Prior to	Murphy	Bergantz	N

Fileno	Title	Auth	To	In
	Design of Hot Pile			
CF-46-2-399	Myrnalloy Report, Book 1			N
CF-46-3-490	The Preparation of Alclad Uranium-Aluminum Alloy	Grenell, L.H.		N
CF-46-4-130	Report of Visit to National Bureau of Standards and to Mr. Louis Jordan of National Research Council Regarding High Temperature Steels or Alloys	Robertson	Willard	
CF-46-4-352	Chapter XI - The Corrosion of Uranium Alloys	Brugman		N
CF-46-5-171	Photomicrographs of Sections of the Product 25 Aluminum Alloys	Grenell	Kyger	N
CF-46-5-360	10.3 - The Partition of the Fission Products Between the Phases of U Alloys	Spedding		N
CF-46-5-598	Myrnalloy Report - Book 2			N
CF-46-6-358	Summary of Information Available on Special Thermo-Couple Wire for Neutron Thermopile and Boron Containing Alloys for Control Rods	Robertson	Willard	N
CF-46-6-438	Myrnalloy Report - Book 3			N
CF-46-7-139	Cover Letter of X-Ray of Ingot and Density Determination of Aluminum Tuballoy Alloys	Saller	Smith	N
CF-46-7-418	Myrnalloy Report, Book 4			N
CF-46-8-381	Myrnalloy Report - Book 5			N
CF-46-9-139	Regarding Aluminum Alloy Ingots	Grenell	Kyger	N
CF-46-9-396	Transfer of Myrnalloy Slugs from Hanford on 9-16-46	Winters	Murphy	N
CF-46-9-417	Uranium Recovery from Al-U Alloy	Milford, R.P.	Eister, W.K.	N
CF-46-9-421	Myrnalloy, Book 6			N
CF-47-1-297	Transfer of Myrnalloy Slugs - H.E.W. No. 3-1	Winters	Murphy	N
CF-47-1-430	X-Metal Inventory - Myrnalloy - 12/46	Whitlock, J.R.	Lewis	N
CF-47-10-130	Request for 10 Beryllium Alloy Cylinders Containing U-235	Winters, C.E.	Murphy, E.J.	N
CF-47-10-727	VOID - Preliminary Report on Rolling and Clodding U Al Alloys	Smith	Kyger	N
CF-47-12-636	Heat Transfer to Mercury	Musser, R.J.		N
CF-47-2-332	Concerning Work in Liquid Alloys - MB-LB-105 Document			N
CF-47-2-377	Thermal Conductivity of Beryllium and Beryllium Alloys	Grenell		N
CF-47-3-160	Myrnalloy Inventory	Whitlock	Lewis	N
CF-47-3-188	Letter Re: U-Al Alloys	Rodden	Byerly	N
CF-47-3-456	Intra-Plant Transfer of Myrnalloy Rods	Kyger	Cox	N

Fileno	Title	Auth	To	In
CF-47-4-423	Myrnalloy Requirements for Clinton Laboratories	Fleury	Chapman	N
CF-47-5-295	Irradiation of Al-U Alloys	Wende	Rodger	N
CF-47-6-116	Tuballoy Inventory for 5/47	Whitlock	Lewis	N
CF-47-6-117	Myrnalloy Inventory for 5/47	Whitlock	Lewis	N
CF-47-6-475	Myrnalloy Record, Book 15			N
CF-47-7-463	Request for Samples of U-Al Alloy	Siegel	Murphy	N
CF-47-8-115	Request for Authorization for Use of Enriched Uranium-Aluminum Alloy	Winters, C.E.	Cook, R.W.	N
CF-47-8-345	Request No. 41 (Cu-Ao Alloy)	Winters, C.E.	Murphy, E.J.	N
CF-47-8-495	Myrnalloy Inventory Technical Division 7/47	Whitlock		N
CF-47-8-602	Myrnalloy Report, Book 17			N
CF-47-9-603	Re: Clad Aluminum Alloy	Grenell	Kyger	N
CF-47-9-621	VOID - Uranium Recovery from Al-U Alloy - Semi-Work Problem Assignment			N
CF-47-9-642	Myrnalloy Report, Book 18			N
CF-48-4-126	Procurement of Myrnalloy Nitrate (Request ORNL-354)	Rucker, C.N.	Belcher, F.H.	N
CF-48-6-146	Preparation of BeU Alloys	Kaufman, A.R.	Hurst, L.K.	N
CF-49-11-77	Draft Copy "Purex Process - 23 Process"	Greene, A.G.	Eister, W.K.	N
CF-49-12-140	Enriched U-Zr Alloy Samples	Holland, A.H., Jr.	Rucker, C.N.	N
CF-49-12-145	Request for Authority to Return Scrap Compounds and Alloys of Beryllium to Production Channels	Rucker, C.N.	Holland, A.H., Jr.	N
CF-49-2-194	Irradiation of Cobalt Alloy - Chalk River	Holland, A.H.	Rucker, C.N.	N
CF-49-4-233	Re: Shipment of Binary Alloys of Uranium	Savidage, R.E.	Boyle, E.J.	N
CF-50-1-84	Fabrication of U(sup 235)-Aluminum Alloy...	Holland, A.H., Jr.	Rucker, C.N.	N
CF-50-10-182	Heat Capacity of Potassium and Three Potassium-Sodium Alloys between 0 Degrees and 800 Degrees C	Douglas, T.B.		N
CF-50-3-216	Corrosion Tests on Various Alloys in Ammonium Bifluoride Solutions	English, J.L.	Jones, D.T.	N
CF-50-4-36	Radiation Stability of Uranium-Aluminum Alloy	Templeton, L.C.		N
CF-50-6-175	Fabrication of Enriched Alloy...	Holland, A.H., Jr.	Larson, C.E.	N
CF-50-6-197	Fabrication of Enriched Alloy Washers...	Holland, A.H., Jr.	Larson, C.E.	N
CF-51-10-120	Results of Mass Analysis on Enriched U-Al Alloys Metal (MTR-Idaho Material) ORNL-CYT-273	Stringfield, H.F.		N
CF-51-10-155	Results of Mass Analysis on Enriched U-Al Alloys Metal (MTR-Idaho Material)	Stringfield, H.F.	Cunningham, J.E.	N

Fileno	Title	Auth	To	In
	ORL-CYT-278 and ORL-CYT-279, IC-583			
CF-51-10-191	Recovery of Uranium from Uranium Zirconium Alloy	Baker, M.		N
CF-51-10-81	Request for Addition Pile Data on Material Covered by Transfer Series Hge-ORL 57,10-24-49			
CF-51-2-176	Quarterly Report - Purex Process	Flenary, J.R.	Steahly, F.L.	N
CF-51-2-38	Improvementof Decontamination in Purex...	Zebrowski, E.J.L.	Bruce, F.	N
CF-51-5-168	Drafts of Purex Pilot Plant Waste Stream...	Darby, D.O.	Organ, E.	N
CF-51-8-182	Results of Mass Analysis on Enriched U-Al Alloy Metal (MTR-Idaho Material) ORL-CYT-251, IC-583	Stringfield, H.F.		N
CF-51-9-4	Additional Results of Mass Analysis on Enriched U-Al Alloy Metal (MTR Idaho Material) ORL-CYT-251	Stringfield, H.F.		N
CF-52-10-60	Plutonium and Uranium Recovery by the Purex Process	Flanary, J.R.		N
CF-52-11-241	A Physical Inventory of the Purex Pilot Plant SF Materials	Sadowski, G.S.		N
CF-52-12-100	Information on Mercury Handling	Schaffer, W.F.	Culler, F.L.	N
CF-52-12-104	Thorex Committee Meeting No. 22, 12-12-52	Ullmann, J.W.	Steahly, F.L.	
CF-52-12-27	Metallography of Thorium and Thorium Base Alloys	Gray, R.J.	Kehl, G.L.	N
CF-52-12-96	Re: Foil of Alloy Containing 8 Atomic Percent Al	Coffinberry, .S.	Shull, C.G.	N
CF-52-8-121	Orex Report for Week Ending July 31, 1952	Blanco, R.E.	Bruce, F.R.	N
CF-52-8-167	Metallurgy of Titanium and Titanium Alloys	Miller, E.C.		N
CF-52-8-171	Orex Planning Committee Meeting, August 14, 1952	Blanco, R.E.	Steahly, F.L.	N
CF-52-8-222	Purex Development Quarterly Report - 5/10 - 8/10/52	Castner, S.V.	Flanary, J.R.	N
CF-52-8-44	Proposal for Study of a High Saturation Purex Flowsheet	Reilly, V.J.		N
CF-52-9-26	Summary of Analytical Procedures for Thorex	Mattern, K.L.	McVey, W.H.	N
CF-52-9-61	The Purex Process	Zebroski, E.L.		N
CF-52-9-88	Orex Process - Equipment List for Chemical Reflux			N
CF-53-10-263	Thorex: Building 3019 Sampler Facility Tentative Design Criteria	Shank, E.M.	Bottenfield, B.F.	N
CF-53-11-11	Rough Draft of Analytical Chemistry for Progress Report, Alloy Development	Kelley, M.T.		N

Fileno	Title	Auth	To	In
	Project, OREX Process, July 1 through September 30, 1953			
CF-53-11-207	Elex and Colex Fundamental Studies through 11-1-53	Clark, W.E.		N
C 53-12-177	Colex Kinetics Studies	Knahn, N.A.	Garretson	N
CF-53-12-86	Status of the Work on the Assignment for ORNL - Uranium-Iron Alloy	Gray, R.J.	Kehl, G.L.	N
CF-53-2-178	The Purex Process at KAPL	Zebrowski, E.L.		N
CF-53-5-15	Comparison of Casts for 10x DT Orex and 10x CR Orex....	Moore, J.A.	Culler, F.L.	N
CF-53-5-164	Orex Program Report for the Quarter Ending March 31, 1953	Drury, J.S.	Clewett, G.H.	N
CF-53-6-168	Two Letters - Colex Process	Oriolo, D.J.		N
CF-53-7-175	Information Available for Design Basis of a Colex...	Oriolo, D.J.	Culler, F.L.	N
CF-53-7-180	Rough Draft of Analytical Chemistry Section for Progress Report Alloy Jan. to Mar.	Kelley, M.T.		N
CF-53-7-181	Rough Draft of Analytical Chemistry Section for Progress Report Alloy April to June	Kelley, M.T.		N
CF-54-10-186	Thorex Sampler Evaluation and Adjustment	Landry, J.W.	Shank, E.M.	N
CF-54-10-187	Thorex: Sampler Evaluation	Landry, J.W.	Shank, E.M.	N
CF-54-11-124	Orex Test Facility Terminal Report	Lindauer, R.B.		N
C 54-12-71	Thorex Report	Bruce, F.R.		N
C. 54-2-204	Chapter X of Zirconium Alloy Systems	Hayes, E.T.		N
CF-54-4-44	Orex: Unit Operations Status Report ...	Jealous, A.C.	Culler, F.L.	N
CF-54-6-119	Orex: Preliminary Report on Run No. 8	Lindauer, R.B.	Johnson, W.N.	N
CF-54-6-120	Orex: Preliminary Report on Run No. 9	Lindaure, R.B.	Johnson, W.N.	N
CF-54-6-17	Orex: Preliminary Report on Run No. 7	Lindauer, R.B.	Johnson, W.N.	N
CF-54-6-254	Comparison of the Thorex and Redox...	Gresky	Shank, E.M.	N
CF-54-9-249	Thorex Critical Construction Schedule	Shank, E.M.	Culler, F.L.	N
CF-55-1-69	Current Status of Thorex Pilot Plant	Culler, F.L.	English, S.G.	N
CF-55-12-16	Request for Uranium Alloys, IC-1402	Swartout, J.A.	Roth, H.M.	N
CF-55-2-164	Abstract - Uranium-Zirconium Fuel Alloy Behavior	Willis, A.H., Jr.	Jetter, L.K.	N
CF-55-2-166	Abstract - Heat Treatment, Hardness and Microstructure of Some Zirconium-Rich Zirconium-Uranium Alloys	Bishop, S.M.	Jetter, L.K.	N
CF-55-3-194	Proposed Research Program - Alloys of Uranium			N
CF-55-3-195	Proposed Research Program - Evaluation of Alloy Prop...			N

Fileno	Title	Auth	To	In
CF-55-3-37	Summary, Metallex Process Dev., Jan. 15-Feb. 25, 1955	Marinsky, J.A.	Katz, W.E.	N
CF-55-4-1	Thorex Program - SF Status #2	Shank, E.M.	Stringfield, H.F.	N
CF-55-5-134	Results on Static Corrosion Tests on Various Nickel-Base Brazing Alloys Used to Fabricate Type 304 SS and Inconel T-Joints	Leitten, C.F., Jr.	Manly, W.D.	N
CF-55-6-178	Results of Static Corrosion Tests on Various Nickel-Base Brazing Alloys Used to Fabricate Type 310 Stainless Steel T-Joints	Leitten, C.F.	Manly, W.D.	N
CF-55-7-119	Status of the Metallex Process	Dean, O.C.		N
CF-55-8-212	Thorex Program SS Status No. 3	Shank, E.M.		N
CF-55-8-60	Metallex Weekly Report	Marinski, J.A.	Mason, E.A.	N
CF-55-8-81	Uranium-Zirconium Fuel Alloy Behavior	Willis, A.H., Jr.	Jetter, L.K.	N
CF-56-1-11	Pulse Column Extraction and Stripping Studies for the Second Thorium Cycle of the Thorex Process	McNamee, R.J.		N
CF-56-1-196	Thorex, Thorium and Thorium Metal Specifications Report	Ferguson, D.E.		N
CF-56-12-126	The Reactor Handbook, Volume III Part C - Cladding and Structural Materials Chapter 25 - Cobalt-Base Alloys	Bridges, W.H.		N
CF-56-3-20	Metallex Process	Dean, O.C.	Runion, T.C.	
CF-56-4-155	Thorex Data	Jealous, A.C.		N
CF-56-5-11	Thorium Alloys	Metko	Saller, H.A.	N
CF-56-7-74	Thorex Data		Jealous, A.C.	N
CF-57-10-40	HRP Radiation Corrosion Studies: Effect of Uranium in Zircalloy 2 Scale	Davis, R.J.	Bohlmann, E.G.	N
CF-57-11-22	Thorex Short Cooled Processing	Meservey, A.B.	Distribution	N
CF-57-11-35	Thorex Pilot Plant Run ...	McDuffie, W.F.	Culler, F.L.	N
CF-57-2-150	Research on Heat Resistant Alloys Strengthened at Elevated Temperatures by the Incorporation of Fine Particulate Substances Prepared under BU of Aero Contract No. 57-400-c		Manly, W.D.	N
CF-57-4-152	Thorex Pilot Plant - Run CF-12 - Summary	McDuffee, W.T.		N
CF-57-4-153	Thorex Pilot Plant - Run CF-13 - Summary	McDuffee, W.T.		N
CF-57-4-2	Criticality Study - A Thorex Pilot Plant..	Yarboro, O.O.		N
CF-57-7-133	Thorex Pilot Plant Run C 7-14 Summary	McDuffee, W.T.		N
CF-58-10-43	Explosion of EBWR Alloy in...	Baird, F.G.	Culler, F.L.	N
CF-58-11-42	An Evaluation of the Design and Performance of the Thorex Pilot Plant	Winsbro, W.R.		N

Fileno	Title	Auth	To	In
CF-58-12-68	Lead-Lithium Shielding Alloy - ...	Frye, J.H., Jr.	Howe, J.P.	N
CF-58-3-124	IC-1685 - Thorex 57-58	Stringfield, H.F.		N
CF-58-3-9	VOID - Thorex Pilot Plant Hydrochlone...	Green, N.D.		N
C- 59-3-11	VOID - High Speed Mercury-Switch, etc.	DeLorenzo, J.		N
CF-59-8-119	High-Temperature Properties and Alloying Behavior to the Refractory Platinum-Group Metals	BMI to Dept. Navy,		N
CF-60-10-108	Collection of Papers Presented and Prepared at ORNL for the Thorex Pilot Plant Program	Shank, E.M.		N
CF-60-7-67	Fission Product Recovery Program Strontium and Rare Earth Extraction - Purex 1 WW with D(sub 2)	Wischow, R.P.		N
CF-61-5-122	Effects of Radiation on the Stress-Rupture Properties of High Temperature Structural Alloys - Contribution to the 12th Meeting of the High Temperature Fuels COmmittee, Held at BMI, May 23-25, 1961	Robertshaw, F.C.		N
CF-61-6-109	Effect of Alloying Elements on the, etc.	Hobson, D.O.		N
C- 63-11-65	Industrial Hygiene Quarterly Report 3rd Oct. '63	Bolton, N.E.		N
CF-64-12-9	Reactor Fuel Alloy	Kleinsteuber, A.T.	Lowry, C.	N
CF-70-10-51	Curium-244 - Iridium Alloy as a Fuel Form	McHenry, R.E.	Lamb, E.	N

McLAREN/HART
MEMORANDUM

To: Dose Reconstruction Team Members (Tasks 1, 2, 4, 5, 7)
From: Gretchen Bruce
Subject: X-10 Records Center Systematic Review
Date: June 24, 1996

Young Moon and I are in the process of conducting a systematic review of records in the X-10 Records Center. This document center consists of inactive records stored in the following three rooms:

Lab Records Storage Center: Room H-204 (Capacity appx. 3,000 cu ft.)
- Box Nos: 962 - 2511
  3315 - 3434
- Directors Files
- Personnel Clinical Files
- ORAU Medical Files

Lab Records Storage Center: Room A-208 (Capacity appx. 1,400 cu ft)
- All "A" Boxes
- All "T" Boxes
- Up to 463
- Medical X-rays

Lab Records Storage Center: Room A-224 (Capacity appx. 1,300 cu ft)
- Box Nos: 464 - 961
  2512 - 3314
- Fulkerson files in cabinets

Records in these rooms are indexed in the BLUREC database as well as in the technical notebook author cardfile located in the X-10 Record Center.

Young and I have completed a systematic review of all non- Privacy Act records in Room H-204 (the room just around the corner from Lab Records). Young is scheduled to review the Privacy Act information within the next couple of weeks. We should complete our systematic review of records in Rooms A-208 and A-224 within the next 2-3 months.

For your information, the following is a summary of the data of potential interest to Dose Reconstruction that we have identified during review of records in Room H-204. With the exception of the items identified in #2 and #4, no copies of any of these materials have yet been requested.

1) Boxes #1087 - 1095 and 2267-2270 (13 boxes total) (Radiochemical Analysis Reports and Records from the X-10 Analytical Chemistry Division, Data for 1986 to 1988). These boxes include analytical data sheets and chain-of-custody type-forms for radiochemical analyses of samples from a number of media including water (e.g., White Oak Creek and White Oak Dam), air (stack sampling and ambient), soil, fish, vegetation, and milk (including analyses for I-131 and Sr-90). Also, Box #2271 contains Sample Log Books for the above samples. Though fairly recent data, may be of interest to **Tasks 1 and 4.**

2) Boxes #1432, 1435, 1436, and 1437 (Environmental Samples Analysis Reports and Backup Data for 1988-89). These boxes include analytical data sheets and COC-type forms for analyses of mercury in a number of environmental matrices, including fish in Watts Bar Lake (including analyses requested by B.G. Blaylock) and air and water (including analyses requested by R. Turner). A sampling of these data was selected for copying. These boxes also include some data for other stable metals, including As, Cd, and Pb, but most is for Total Organic Carbon and miscellaneous anions and cations. Of interest to **Task 2** and of possible interest to **Task 7.**

3) Boxes #962-968 (7 boxes) (Environmental Waste and Analytical Data from 1961-78). These boxes include water and air release data from the Settling Basin, ORNL stacks, etc. for I-131 and other radiological parameters including Cs-137, Sr-90, etc. Box #962 appears to be the most useful- data include weekly summaries of ORNL waste discharges from intermediate-level waste, process waste, and from stacks, as well as waste volumes. The other boxes include analytical data report sheets for radiological analyses, but it was not immediately apparent where these data were collected. Of possible interest to **Tasks 1 and 4.**

4) Miscellaneous memos/reports largely from the Subject Files (these are files boxed by year and specific category, and are the same type of material as in the Director's Files, i.e., correspondance to/from division directors). Copies were requested of a number of items including memos re: PCBs in transformers at ORO facilities, WOD monitoring data, a Sr-90 release in 1985, a Cs-137 release in 1986, mercury monitoring at ORNL, and ORNL stack releases. Of possible interest to **Tasks 1, 2, 3, 4, and 7.**

If you are interested in any of the material summarized in #s 1, 2, or 3, I recommend that a member of your Task team review the material in person. A member of the X-10 Lab Records staff can pull specific boxes for your review (contact either me or Young Moon for more information).

CLARIFICATIONS FROM GRETCHEN

sources before WOD, not at WOD

V. Little 60's

H_2O 60's

ChemRisk Repository Number: 2540
Title: "Interview Notes: Stanley Rimshaw"
Authors: Shonka, J. J., Widner, T. E.
Abstract: Stanley Rimshaw was interviewed at his home by the Oak Ridge Dose Reconstruction team on April 28, 1995 at 1430 hours. Mr. Rimshaw's address is 304 Dominion Circle, Knoxville TN 37922. The interview came after the ORHASP meetings, and the briefing binder used at the ORHASP meeting on the RaLa process was available. It contained the operations manual and photographs of the 706D building and equipment. These proved useful for stimulating discussion. Mr. Rimshaw was interviewed for Task 1, since he was the shift supervisor of the RaLa chemists. Mr. Rimshaw had a Bachelor's degree in Chemistry prior to coming to Oak Ridge in 1943. One of his professors in college was Kistiakowski, and he recalled discussion while in college in 1939 of the German discovery of fission and its implication. Prior to coming to Oak Ridge, Mr. Rimshaw worked for DuPont in explosives in a plant in Oklahoma. He worked primarily in the acid end of the process, doing nitration of cotton. He was hired by the Manhattan Engineering District because of his education. In 1943, he was tasked to help startup the graphite reactor. Following startup, the X-10 site was beginning to divide into groups. Because of his background, Mr. Rimshaw then joined the Hanford Pilot Plant Program, which used a lanthanum fluoride carrier to separate plutonium from uranium. The process output was a steel bucket containing plutonium that was delivered to the plutonium chemist. He later joined the radioisotope program, which performed a number of small processes. P-32 was separated in a small lab on the side of 706C (in 706D toward the "C" end); some Sr separations; Ru distillations from oxidizing solutions, etc. He once held a beaker up to this ear in which P-32 was undergoing a funny reaction and got his head contaminated. It was washed off when he stepped into the shower. Essentially, processes were tested out "anywhere there was a hood". Radiation control for workers was accomplished by working out in the open with small amounts using distance to control radiation exposures. They did not work with full amounts unless the engineers designed a system for it. Mr. Rimshaw was appointed as a shift supervisor for RaLa. The RaLa process involved separation of an alkaline earth (barium) from a rare earth and letting the lanthanum grow in from the barium. The dissolution step used a mercury catalyst with nitric acid. It was conducted in periodic campaigns, with two or three shipments per campaign. Most of the occupational exposure came from decontamination operations. Staff was limited to 100 mR per day and decontamination used fire hoses to hose down the process from above. The first was not sent directly to the gunnite tanks. He received lifetime exposure of 60R, one-half of which or more came from RaLa decon operations. They began to hire operators to run the operations. A straight shift would be organized, when needed. The shift information would be logged in logbooks. Between runs, the operators would be trained. Iodine releases were not their concern, but came under the jurisdiction of health physics. Bob Schaich, who was the overall RaLa manager, insisted on a very tightly controlled operation. There were few accidents that he could recall associated with RaLa. He did recall a formaldehyde explosion on the hill during the war years. Also, because of their process chemistry expertise, they were called on following an accidental release to mix caustic and alum and disperse the solution onto a pond outside of the building (not White Oak Lake, but a settling basin) to precipitate out fission products (mostly cesium) reducing the dose rate. This was an experiment and not routine practice. When asked about the 1949 plane flight that observed a plume a distance from

X-10, Mr. Rimshaw did not recall anything extraordinary about the run (i.e., that is was not intentionally larger than normal). They

865	145	0004508700	Cutoff Saw			N	Y	N	$2,635.00
865	145	0004508800	Shears		BM6404	N	Y	N	$2,400.00
865	145	0007896800	Impact Tester		522995	N	Y	Y	$1,483.78
865	145	0008965300	HIP Control		M8702452-1	Y	Y	Y	$681,361.74
865	145	0009906900	Monitor	IBM	3575113	Y	Y	Y	$500.00
865	145	0012599100	Lube Cart		930687208037	N	Y	Y	$1,840.00
865	145A	00038267R0	Computer	Digital	2314A07986	N	Y	Y	$36,267.00
865	148	0003824200	HIP Pressure Vessel			Y	Y	Y	$19,149.96
865	148	0003829400	Furnace	HIP		Y	Y	Y	$5,000.00
865	East	0003838100	Fire System CO2			Y	Y	Y	$161,440.00
									$5,622,070.99

had a lot of alum around for doing fission product plant chemistry with rare earths, strontium, and plutonium. Most of the constituents that are carried on alum constitute the main part of the radiation from fission products. He left the RaLa program in 1956. After the war years, he became the group leader of the radioactive isotope production program. The research in the early years was basically investigating the periodic table and what could be created. The group took every mineral in the book and irradiated it to see what they would get. They produced kilocuries of cesium and promethium, the latter for use as a source of radiation similar to a portable X-ray machine. The most challenging chemistry was for ruthenium. Ruthenium reacts to give an extremely small AMAD particle, which is difficult to filter. Schaich ran the fission product plant. The RaLa production runs were not timed to take advantage of favorable weather. A lead process was used to precipitate out the barium. It was converted then to a carbonate. The uranium dissolution off-gas went out to the big stack. Plutonium dissolution would go out the same stack. The short stack was the negative pressure off the cells. The off-gas was extremely acidic, and caustic scrubbers were used to neutralize the gas. Mole for mole, it takes a lot of caustic to neutralize NO3. Brown fumes would come out of the stack. The acid would condense on the stack, and the mortar between the bricks was crumbling away, so X-10 found it necessary to paint the upper part of the stack with asphalt. Because of the hydration reaction, a long contact time is required to neutralize the acid vapors. George Parker, who lives down the street from Mr. Rimshaw, would be more knowledgeable about vent design and iodine and technicium releases. (Rimshaw was more production oriented.) Joe Lewin (Oak Ridge) designed scrubber systems, including the one on the north side of X-10 near the road. Mr. Rimshaw was unaware of any involvement of ORINS in measuring RaLa releases. He recalled a separate test that was conducted, where an experiment was installed in the stack. John Gillette may have more information concerning this experiment. On 8/21/95, the above write up was sent to Mr. Rimshaw for a technical accuracy review. He was asked to carefully review his assertion that mercury was used as a catalyst in the dissolution process. It was pointed out to him that the RaLa flow sheets made no mention of Hg. He was also asked if the "formaldehyde explosion up on the hill" he mentioned could have been the Nov. 20, 1959, incident in Building 3019 when an evaporator exploded during decon with Turco Decon 4501, releasing Pu to the South of 3019. No written response was received. However, verbally Mr. Rimshaw reasserted that mercury was the catalyst. However, he also asserted that it was used in some of the initial runs where there was no radiation involved (i.e., during the time period early '43 to late '44). Its use was to reduce plutonium to lower valence state. In regard to "formaldehyde explosion", he clarified that it could have been formic acid. He suggested talking with Art Rupp who is in a nursing home in Oak Ridge. Mr. Rupp started the Radioisotope Division. The explosion discussed in the 4th paragraph was not the 11/20/59 event in Building 3019, but was a chemical reaction which pressurized a tank when a new hiree accidentally pumped concentrated reducer and oxidizer into the tank. Mr. Rimshaw recalled that the consequences were minor. Mr. Rimshaw also offered details about the release to the settling pond that was discussed in the interview. The incident was caused by a leaking cooling water coil in the dissolver vessel. Cleanup was an adhoc process that included use of clay to find cesium, rather than a precipitation process.

Reviewer: Shonka, J. J.

Building	Room or location	Capital Equipment Number	Description	Manuf
865	106	0000026500	Transducer	
865	106	0000243400	Electronic Power Controller	
865	106	0001895500	Hardness Tester	
865	106	0001924300	Hardness Tester	Brinnell
865	106	0003321900	Hardness Tester	Wilson
865	106	0003672000	Loader for 8" Grinder	
865	106	0003825800	Hardness Tester	
865	106	0003825900	Hardness Tester	
865	106	0003827900	Grinder Polisher	Jarrett
865	106	0003830000	Grinder	
865	106	0003830100	Fume Hood	Aerostrear
865	106	0003835600	Recorder	
865	106	0003836900	Polisher	Vibromet E
865	106	0003838200	Grinder - Specimen	
865	106	0009864200	Polisher	Vibromet
865	106	0009864300	Hardness Tester	Clark
865	108	0003818500	Control Variable Speed	
865	108	0003827700	Transducer	
865	108	0003834600	Instron	
865	108	0009864700	Instron	
865	136	0001316400	Saw	
865	136	0001819100	Rotary Table	
865	136	0001899400	Lathe	
865	136	0001900500	Lathe	
865	136	0001912500	Lathe Tracer	
865	136	0001915700	Grinder	Brown & S
865	136	0001918200	Mill	
865	136	0001926100	Lathe	Hardinge
865	136	0001927300	Mill	
865	136	0001927400	Optical Comparator	
865	136	0001931100	Lathe	
865	136	0003815000	Bridge Crane	
865	136	0003815300	Lathe	
865	136	0003817000	Tracer Lathe Mimik	Hardinge
865	136	0003817200	Band Saw	Mati
865	136	0003819600	Motor	
865	136	0003826000	Mill	
865	136	0003826100	Lathe	
865	136	0003830200	Amplifier	Brown and
865	136	0003836800	Lathe	
865	136	0003841800	Vacuum Cleaner	

Date Document Issued: 04/28/95
Classification Category: UNC

Distribution

1-4.E. J. Murphy
5.Dr. Walter Wilkinson, ANL
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ABSTRACT

59-7-60

Cleared by Eggert Patent 7/21/59

THE USE OF MERCURY IN REPROCESSING NUCLEAR FUELS

by

O. C. Dean
A. F. Messing
H. C. Forsberg

Oak Ridge National Laboratory
Oak Ridge, Tennessee
Operated by
Union Carbide Corporation
for the
U. S. Atomic Energy Commission

to be presented at the
AIME Meeting, New York City,
February, 1960

THE USE OF MERCURY IN REPROCESSING NUCLEAR FUELS

(O. C. Dean, A. F. Messing, H. C. Foreberg)

Uranium, thorium and plutonium form series of intermetallic compounds with mercury of low stability. Although these intermetallics are quite pyrophoric, they are wetted and protected from oxidative atmospheres by excess mercury. The uranium-mercury compound UHg_4, which is stable at one atmosphere at temperatures below 365°C, is soluble in mercury up to 1.2 atomic per cent uranium at 356°C. The plutonium compound is nearly as soluble, but $ThHg_3$ is about one order less soluble. Since the noble fission products, e.g., ruthenium and molybdenum have mercury solubilities from two to 5 orders less than uranium, good separations may be obtained. The more soluble alkaline earths and rare earths are oxidized preferentially and their oxides are not wetted by mercury, so they can be filtered from the hot uranium solution.

Uranium and thorium are readily recovered from mercury. The mercurides crystallize and can be filtered from solution at 25°C. Vacuum distillation at 800°C removes the remaining mercury to <10 ppm. The uranium may be melted in the same retort, but thorium appears as massive, but porous sintered billet with a density of ~ 75% of theoretical.

The chlorides of uranium and thorium have been reduced to their respective mercurides by alkali metal amalgams. Impurities have been eliminated from the amalgams by washing, and the massive metals have been recovered. Uranium hexafluoride has been reduced to UHg_4 with lithium amalgam and the uranium recovered with a yield of >80%.

The phase relationships in the mercury-uranium and mercury-thorium systems have been studied. A corrected phase diagram and the thermodynamic properties have been worked out for the uranium system. A tentative phase diagram is presented for the thorium-mercury system. Solubilities of ruthenium, palladium, molybdenum and zirconium in mercury saturated with uranium have been determined. Solubilities of gadolinium, neodymium, samarium, uranium and thorium in mercury have also been determined. Decontamination factors for major fission products from uranium metal on a 100-gram scale range from 10 to 10^4.

March 12, 1943

WEEKLY SUMMARY REPORT
WEEK ENDING MARCH 11, 1943

Solubility of Uranium Coating Alloys in Nitric Acid Containing Mercuric Nitrate

Tests were carried out to see if the dissolving of aluminum in nitric acid containing 0.1% mercuric nitrate produced any explosive gases. These tests were performed in a glass bottle with a spark gap in the gas stream. The spark was run continuously during the solution and was provided by a Tesla coil. The acid strength used was 45% with an amount of aluminum roughly corresponding to the proportion of aluminum to acid contemplated for the plant scale. No sign of an explosion could be observed. The tests were repeated while passing an air current through the apparatus in order to make sure that enough oxygen was present to combine with any hydrogen that might be evolved. There was no sign of any explosion.

Tests were continued on the rate of solution of aluminum in various strengths of nitric acid all containing 0.1% mercuric nitrate hemihydrate. Solution was effected at the boiling point. A very sharp break in the rate of solution was found between 52 and 53% nitric acid strength.

	Time to dissolve a strip 0.02" thick strip acting from one side only.
40%	8 min.
44.5%	19 "
44.5%	15 "
50%	17 "
52%	42 "
53%	286 "
53%	283 "
60%	277 "

Aluminum strips were immersed in nitric acid samples of 40, 44.5 and 50% strengths each containing 0.1% mercuric nitrate at room temperature. After two days solution has not been effected.

Program -

Samples of nitric acid containing mercury salts corresponding to the starting solution and spent acid containing metal nitrates corresponding to the solution after the metal has been dissolved are being prepared for corrosion tests on stainless steel elsewhere.

A sample of zinc alloyed with 6% aluminum which is proposed as a coating material has been received and will be tested for dissolving properties.

J. V. P. Torrey

A-670

[redacted] 35 44-8-737

File

Date 8-25-44

Subject CASE NO. S-1432 (USE OF HG AND CE FOR GAMMA DECONTAMINATION)

By Evans

To Doan

Those Eligible To Read the Attached

Copy 1 Doan

INV. 62

Inv. 61

INV. 63

RECEIVED AUG 28 1944 R. L. DOAN

Before reading this document, sign and date below

Name	Date	Name	Date

Inv. 67

INV. 64

CLASSIFICATION CANCELLED

DATE AUG 1 1 1977

H. L. McDuffie

DECLASSIFICATION OFFICER

OAK RIDGE NATIONAL LABORATORY

AUTHORITY DELEGATED BY AEC 7-15-71

[redacted]

mke 8-24-78 cl 98

ARMY SERVICE FORCES
UNITED STATES ENGINEER OFFICE
MANHATTAN DISTRICT
OAK RIDGE, TENNESSEE

IN REPLY REFER TO EIDMF-1-a
MD 070

25 August 1944

Dr. R. L. Doan
Clinton Laboratories
Oak Ridge, Tennessee

Re: S-1432

Dear Dr. Doan:

Transmitted herewith for your information and files is a copy of the disclosure in the above-identified case.

Very truly yours,

SYLVESTER M. EVANS
Advisor on Patent Matters
Oak Ridge Patent Group

Incl:
Disclosure

[redacted]

DISCLOSURE

OSRD CASE NO.: S-1432

INVENTORS: B. F. Faris & H. K. Strassel

SUBJECT: Use of Hg and Ce for gamma decontamination

OBJECT: To improve processes for decontamination and product precipitation with carriers by the use of certain supplemental addition agents such as mercury and cerium compound.

DESCRIPTION: The description of the process of using mercury and cerium compounds is the same as that set forth in Abstract dated 9 May 1944.

PRIOR ART: Published: None known
Related art on project: See Reports MCN-1409 and 1425 referred to in Abstract.

PROBABLE VALUE: The process has been tested experimentally and while improvement is indicated, the apparent improvement over existing procedure appears to be of insufficient magnitude to warrant the changing of existing practice. Consequently, it is not expected that the process will be used unless unforeseen difficulties are encountered in future operations.

RECOMMENDATIONS AND COMMENTS: The proposed process represents a potential alternative method which could be utilized in the event difficulties are encountered in gamma decontamination. Providing a search indicates novelty, a patent application may be warranted on this alternative procedure.

PROPOSED CLAIM: In processes for recovery of Pu from solutions containing gamma contamination, by procedure utilizing carrier precipitate for by-product and product separation the improvement feature of supplementing the carrier precipitates' action by the use of mercury and cerium compound additions.

Author: H. N. Powell

Date: 25 August 1944

Approved by: Sylvester M. Evans

OP-59 Revised

Rec'd w/o 11-18-66

SECRET

CENTRAL FILES NUMBER 3-29-24 N5-7-476

PROJECT 9536

Dep. Gen.

Route List

1. ~~R.N. Smith~~
2. ~~D.J. Hanahan~~
3.
4.
5.

File

Date 7-26-45

Subject Summary of the Work on the Mercury Cathode.

To B.F. Butler

From R.E. Kitson

Copy No. 3

R.N. Smith
D.J. Hanahan

BEFORE READING THIS DOCUMENT, SIGN AND DATE BELOW:

HANFORD ENGINEER WORKS
RECEIVED
JUL 1 1945

INV. 64

SECRET

CC: 1. B. F. Butler
2. G. W. Struthers-R.E.Curtis
3. R. N. Smith-D. J. Hanahan
4. R. E. Kitson-E. I. Martens
5. 300 File Copy
6. 700 File Copy
7. Pink Copy
8. Yellow Copy

3-2 80;

US-21033

750 REAMS 2065 3-44 ROS

INTER-OFFICE MEMORANDUM

ORNL

CENTRAL FILES NUMBER

To: B. F. BUTLER

Date July 26, 1945.

Subject SUMMARY OF THE WORK ON THE MERCURY CATHODE DONE BY JAMES FENTRESS BETWEEN JANUARY AND JUNE, 1945.

4 3 8 A

Attached is a brief summary of the work on the mercury cathode done by James Fentress between January and June, 1945.

Originally, this work was undertaken to provide a method for the separation of iron and uranium. It was ultimately extended to a variety of problems. At the present time, unfortunately, it has fallen into disuse. On a micro or drop scale, the equipment involved requires some technique to remain in satisfactory operating conditions. On any scale the precision obtained is not as great as that ob--tainable in usual titrimetric determinations. We are now accumulating on independent investigations, evidence to indicate that most titrimetric methods for uranium and plutonium methods are not precise, because of the high equivalent weights involved.

We believe that the mercury cathode possesses a great potentiality in analytical chemistry. It should prove particularly valuable in the determination of uranium.As soon as manpower is again available, we hope to resume the study of this method.

Subsection A

R E Kitson
R. E. Kitson

peb

THE MERCURY CATHODE

In the analytical chemistry of uranium one of the most difficult separations is the separation of uranium from iron. Iron, which causes serious errors in the volumetric determination of uranium, is usually removed by precipitation in basic solution. If the precipitation is carried out with ammonium carbonate the uranium remains in solution as the soluble double carbonate and the insoluble ferric hydroxide is filtered off. This method is both long and subject to error due to the character of the iron precipitate. Further, any method involving a separation by precipitation would be almost useless for any 200-Area method.

It, therefore, became necessary to develop a method, applicable even on a micro-scale, for the separation of iron from uranium. A search of available literature revealed the fact that if a mixture of ferric sulfate and uranyl sulfate in dilute sulfuric acid was electrolyzed using a mercury cathode, the ferric ion would be reduced to metal and discharged on the mercury leaving the uranium behind in solution.[1] No mention was found as to the final condition of the uranium at the end of the electrolysis other than the fact that it remained in solution.

A cell was, therefore, constructed according to Melaven[2] and the electrolysis carried out in 2% sulfuric acid, using a mixture of 1:1 uranyl and ferric sulfate. About 150 grams of mercury was used as the cathode, and a #18 platinum wire as an anode. As a high current density was recommended, a current of about 4 amps., with an e.m.f. of about 8 volts was used. The electrolyses were carried out for 30-90 minutes with samples being taken every five minutes to check iron concentration. It was found that using a "still" cathode, the iron cencentration dropped off until a plateau was reached which was found to represent saturation of the mercury surface. This saturation could be over-come by vigorous stirring of the mercury surface, in which case the rate of deposition of iron followed

closely the expected curve. During the electrolysis no uranium was lost from the solution. Thus, a highly satisfactory means of separating iron from uranium was established. In a later series of experiments on separation of iron from plutonium, similar results were obtained.

It was further found that the uranium which was originally present as the uranyl ion was reduced by the cell to a mixture of the tri - and quadra-valent ions. Since the volumetric determination of uranium depends on reduction of uranyl ion to the uranous state (quadra-valent ion), followed by re-oxidation with a standard oxidizing agent such as potassium permanganate or ceric sulfate, the fact that the reduction takes place in the cell at the same time as the iron is being removed, gave a new short-cut for the uranium determination.

Solutions containing uranyl sulfate in sulfuric acid (no iron) were next reduced in the cell and titrated directly without any further reduction. Recoveries were always on the order to 200% or higher. Since the titration was carried out from quadra - to hexa-valent uranium, and it was known that some tri-valent uranium was present, care was taken to mildly oxidize all tri-valent metal to the quadra-valent stage before the volumetric oxidation was begun. Even with this precaution recoveries were still greater than 200%. After some investigation of the interferring substance it was identified as hydrogen peroxide. This compound was being formed at the electrodes by the high current and was then being titrated by the ceric sulfate.

In order to circumvent this difficulty the form of the anode was changed. A 2 sq. in. platinum foil electrode covered with a deposit of platinum black was used. It was hoped that the large surface of platinum black would serve to catalyze the decomposition of any hydrogen peroxide formed. Results with the new anode were highly satisfactory using uranyl sulfate solutions.

The investigation was next extended to solutions of uranyl nitrate to which small amounts of sulfuric acid were added. Preliminary investigations indicated that the nitrate ion was reduced by the mercury cathode, and

[redacted]

recoveries of uranium were 100± 5%. Appreciable amounts of ammonium ion were found, but no quantitative data was obtained as to the degree of completeness with which the nitrate ion was reduced. No nitrate ion, as such, remained in solution.

With the small amount of evidence at hand it was decided to try the method for routine analysis of uranium on a tentative basis. The laboratories all found that while the accuracy taken on the average of several determinations was good, the precision of the method was not satisfactory.

The method was, therefore, taken back and re-investigated. The reduction of uranyl sulfate solutions were followed potentiometrically, and under standard procedure was found to be normal. There was no evidence of hydrogen peroxide formation, and blank runs on acid solutions gave no reduction. The values for the potentials found experimentally agreed very well with literature values.

Due to lack of time the work was discontinued at this point.

There is no reason chemically to put aside the mercury cathode determination of uranium. The method is capable of giving very satisfactory results if a little more work is done. Of several important points to be kept in mind the following are most critical:

1. The formation of hydrogen peroxide can still be serious if the reduction is so "strong" that the amount of platinum black present is not enough to decompose the peroxide as fast as it is formed.
2. The nitrate ion must be completely reduced to ammonium ion, as intermediate reduction products can give bad results.
3. In using such high current densities the heating effect on the solution is very great, (with micro cells the solutions are almost raised to the boiling point), and effects such as tri-quadra-ion ratios at different temperatures must be investigated. This heating effect is probably the most important and the least is known about it.

James Fentress

James Fentress

1 W. R. Bennett J. Am. Chem. Soc. 56, 277, 1934.

2 A. D. Melaven Ind. Eng. Chem. Anal. Ed. 22, 180, 1930.

peb

H6-11-89

B-137

File D-E-5

Date November 5, 1946

Those Eligible To Read The Attached

Subject Use of the Mercury Cathode for the Purification of Uranium Solutions

Copy # 1

By W. H. Baldwin

To M. D. Peterson and M. T. Kelley

~~Peterson Kelley~~
F. L. Steahly

Before reading this document, sign and date below:

Name	Date	Name	Date
M D Peterson	11/8/46		
M T Kelley	11/12/46		
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Distribution:
1. M.D.Peterson and M.T.Kelley
2. A.F.Rupp
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7. Central Files

November 5, 1946

To; M. D. Peterson and M. T. Kelley

From: W. H. Baldwin

USE OF THE MERCURY CATHODE FOR THE PURIFICATION OF URANIUM SOLUTIONS

It was recently brought to our attention by D. E. Hull, presently in the training school, that the mercury cathode has been used successfully by both Y-12 and K-25 for the purification of uranium solutions in processing and in analytical work. Discussions with workers at Y-12 and K-25 show that limiting conditions have not been examined critically but certain operable methods are known:

1. Acidity - (a) pH4 to 3N H_2SO_4 at Y-12 - 0.3N; at K-25 - 2N

   (b) Nitrate and chloride if present in the cell must be evolved before satisfactory reaction occurs. Removal may take place beforehand or in the cell.

2. Volume of electrolyte used in the laboratory is ordinarily 30 - 50 ml but Y-12 had developed a process to handle up to 10 liters.

3. Agitation - Opinion favors stirring the cathode with minimum agitation in the aqueous layer.

4. Anode Area - Minimized (a platinum hoop near the surface) was suggested to favor rapid escape of O_2.

5. Purity of mercury - highest purity required for speed and completeness of ion removal. Therefore it has been suggested that the mercury be changed either periodically or continuously.

6. Amperage and temperature -
   (a) Y-12 uses at least 10 amps and finds water cooling necessary to prevent explosions resulting from the recombination of H_2 and O_2.

   (b) K-25 uses a lower amperage (3) and has not found water cooling necessary though some workers do use it.

Lundell and Hoffman "Outlines of Methods of Chemical Analysis" claim "quantitative" deposition of Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, 43, Rh, Pd, Ag, Cd, In, Sn, Re, Ir, Pt, Au, Hg, Tl, Bi, Po, As, Se, Te and Os from 0.3 N H_2SO_4 (the last 4 are not quantitatively deposited in the mercury); Mn, Ru, and Sb are quoted as being incompletely deposited.

On the basis of the foregoing information, the mercury cathode should prove valuable for the separation of Fe, Ni and Cr (elements from the corrosion of stainless steel) from isotope preparations (Ba 140, UX_1 etc.).

The present practice at K-25 of using the mercury cathode to purify solutions before plating uranium for counting will be tested with uranium 237 and uranium 233 tracer.

A similar process will be investigated using strippings from solvent extraction to study the decontamination from those elements that follow U through the extraction cycle. By combining the mercury cathode electrolysis step with the plating of uranium it should be possible to achieve further decontamination in the 25 decontamination process.

Distribution: 1. M. D. Peterson and M. T. Kelley
2. A. F. Rupp
3. W. A. Rodger
4. F. L. Steahly
5. R. E. Blanco
6. W. H. Baldwin
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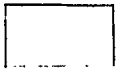
Elements that can be Determined by Electrodeposition

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr 7	Mn 8	Fe 2,7	Co 3,4 7,8	Ni 3,4 7	Cu 1,2,3 4,7	Zn 2,3 4,7	Ga 7?	Ge 7?	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo 6,7	43	Ru	Rh 1,7?	Pd 1,3 7?	Ag 1,3 4,7	Cd 1,2 3,4,7	In 2,4 7	Sn 2,5 7	Sb 1,5	Te 2	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re 1,6,7 ?	Os	Ir 7?	Pt 1 7?	Au 1,4 5,7	Hg 1,4 5,7	Tl 7,8	Pb 1,8	Bi 1,2 7	Po 1,7? 8	85	Rn
87	Ra	Ac	Th	Pa	U 6	Np	Pu	Am	Cm								
*Ce 58	Pr	Nd	61	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu 71				

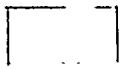
1. On cathode in mineral acid solution.
2. On cathode in organic acid solution.
3. On cathode in alkali solution.
4. On cathode in cyanide solution.
5. On cathode in alkali sulfide solution.
6. On cathode as hydrated oxide in acid solution.
7. On mercury cathode in weak acid solution.
   7? deposition is incomplete - method not described in literature.
8. On anode as hydrated oxide in acid solution.

Lundell and Hoffman - page 168.

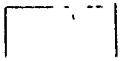
Electrolysis with a Mercury Cathode



Quantitatively Deposited at Cathode



Incompletely Separated



Quantitatively Separated, (but not in Cathode)

ChemRisk Repository Number: 2003 Document Number: ORNL - TM - 568
Title: "Removal of Mercury from Waste Solution Prior to Calcination or Fixation"
Authors: Clark, W. E., Easterly, J. F., Godbee, H. W.
Abstract: Mercury cannot be quantitatively retained in the solid product obtained by calcination-fixation of waste because it forms no compounds which are stable at high temperatures. Attempts to operate a mercury trap in the off-gas line from the fixation pot have been successful in trapping a maximum of about 50% of the total mercury present on both laboratory and unit operations scales. In batch operations it will probably be possible to hold the top of the fixation pot at a relatively low temperature until the final calcination step and then to trap out most of the mercury together with a fraction of rather concentrated nitric acid. This side stream would presumably be sent to a separate waste storage tank for eventual reprocessing in a special campaign. This procedure, while feasible, appears to be unduly cumbersome, and limits the operation of the system to a true batch process. Removal of the mercury from the feed to the evaporation-fixation system appears preferable if it can be accomplished simply and cheaply.
Reviewer: Moon, U. Y.
Document Source or Location: X-10 Laboratory Records
Date Document Issued: 04/24/63
Classification Category: UNC
Site Document Addresses: X
Primary Document Category: HO

Date Entered: 8/16/95
Entered By: SMG
Keywords: mercury
FYI, we have a copy.

Rep. No 2003 from ALA repos.

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ORNL - TM - 568

COPY NO. - 2

DATE - April 24, 1963

REMOVAL OF MERCURY FROM WASTE SOLUTIONS PRIOR TO CALCINATION OR FIXATION

W. E. Clark
J. F. Easterly
H. W. Godbee

ABSTRACT

More than 99.9% of the mercury was removed from Hanford 1965 FTW waste by displacement with copper. The method appears to be quite feasible for all except the more concentrated of the nitrate wastes.

An evaluation of the advantages and disadvantages of the method compared to the operation of a mercury trap in the calciner off-gas line is desirable.

1 of 1 Complete Record
0075657 NSA Accession Number: NSA-12-000154
Title: PAPERS PRESENTED AT THE BELGIUM SYMPOSIUM ON CHEMICAL REPROCESSING, BRUSSELS, MAY 20-24, 1957
Corporate Source: Atomic Energy Commission, Washington, D.C.
Publication Date: nd Page(s): 481 331 364
Primary Report No.: TID-7534
Journal Announcement: NSA12
Availability: NTIS
Document Type: Report
Language: English
Abstract: The papers of the three sessions recorded in book one deal with aqueous reprocessing, auxiliary processes, and disposal of plant effluents. In Aqueous Reprocessing, typic al chemical processes for dissolving and preparing relatively simple fuel elements (Al clad or canned) for solvent extraction treatment are discussed. Typical chemical and process flowsheets for solvent extraction separ;tion and decontamination of U-- Pu in natural U, U/sup 233/--Th from Th, and enriched U from U-Al alloy are presented. Performance characteristics of packed columns in Redox Process, and pulse columns and mixersettlers in Purex Process are given. Auxiliary Processes are those dealing with unusual fuels, converting them to solutions amenable to solvent extraction. The most widely proposed diluents and claddings for these power reactor fuels are Zr and stainless steel, and the various methods for dissolving them are surveyed. Also described as auxiliary processes are methods for additional decontamination from Ru, Zr, and Nb, for concentrating dilute U/sup 233/ and Pu, and for calcining UNH to UO/sub 3/ and converting Pu(NO/sub 3/)/sub 4/ to metal. In Disposal of Plant effluents the methods used for treatment, concentration, storage, and dispersal of gaseous, liquid, and solid wastes from radiochemical processing plants are summarized. After waste disposal problems are treated in general, the treatment of gaseous effluents, preparation of waste for liquid disposal, and the retention of high level radioactive wastes are discussed. The problems of ultimate disposal of radioactive waste to the environment are surveyed with consideration of the development of a nuclear power economy during the next fifty years. Unit costs and economic relationships for some of the better understood stages of the general scheme of waste disposal are derived. Book two, entitled Nonaqueous Processing deals with fluoride volatility processes and pyrometallurgical or pyrochemical processes. The latter involves either an oxide drossing or molten metal extraction or fused salt extraction technique and results in only partial decontamination. Fluoride volatility processes appear to be especially favorable for recovery of enriched U and decontamination factors of 10/sup 7/ to 10/sup 8/ would be achieved by simpler means than those employed in solvent extraction. Data from lab research on the BrF/sub 3/ process and the ClF/sub 3/ process are given and dis cussed and pilot plant experience is described, all in connection with natural U or slightly enriched U processing. Fluoride volatility processes for enriched or high alloy fuels are described step by step. The economic and engineering considerations of both types of nonaqueous processing are treated separately and as fully as present knowledge allows. A comprehensive review of the chemistry of pyrometallurgical processes is included. Engineering and Economics is the title of book three which is concerned with several phases of chemical reprocessing of fuels which are of a general nature. Hot labs, radiochemical analytic al facilities, and high level development cells are described. Dissolution equipment, contactors, flow generation, measurement, and control equipment, samplers, connectors, carriers, valves, filters, and hydrocIones are described and discussed. Papers are included on: radiation safety, chemical safety, radiochemic al plant operating experience in the U. S., and heavy element isotopic buildup. The general economics of solvent extraction processing is discussed, and capital and operating costs for several U. S. plants given. The Atomic Energy Commission's chemic al processing programs and administration are evaluated and the services offered and charges therefor are listed. (T.R.M.)
Descriptors: ALUMINUM ALLOYS; BROMINE FLUORIDES; CHEMICAL REACTIONS;

1 of 1 Complete Record
0075657 NSA Accession Number: NSA-12-000154
Title: PAPERS PRESENTED AT THE BELGIUM SYMPOSIUM ON CHEMICAL REPROCESSING, BRUSSELS, MAY 20-24, 1957
Corporate Source: Atomic Energy Commission, Washington, D.C.
Publication Date: nd Page(s): 481 331 364
Primary Report No.: TID-7534
Journal Announcement: NSA12
Availability: NTIS
Document Type: Report
Language: English
Abstract: The papers of the three sessions reco
aqueous reprocessing, auxiliary processes, and
In Aqueous Reprocessing, typic al chemical pro
preparing relatively simple fuel elements (Al
extraction treatment are discussed. Typical c
flowsheets for solvent extraction separation a
in natural U, U/sup 233/--Th from Th, and enri
presented. Performance characteristics of pac
and pulse columns and mixersettlers in Purex P
Processes are those dealing with unusual fuels,
solutions amenable to solvent extraction. The
diluents and claddings for these power reactor
steel, and the various methods for dissolving
described as auxiliary processes are methods fo
from Ru, Zr, and Nb, for concentrating dilute
calcining UNH to UO/sub 3/ and converting Pu(NO
In Disposal of Plant effluents the methods used
concentration, storage, and dispersal of gaseous, liquid, and solid wastes from radiochemical processing plants are summarized. After waste disposal problems are treated in general, the treatment of gaseous effluents, preparation of waste for liquid disposal, and the retention of high level radioactive wastes are discussed. The problems of ultimate disposal of radioactive waste to the environment are surveyed with consideration of the development of a nuclear power economy during the next fifty years. Unit costs and economic relationships for some of the better understood stages of the general scheme of waste disposal are derived. Book two, entitled Nonaqueous Processing deals with fluoride volatility processes and pyrometallurgical or pyrochemical processes. The latter involves either an oxide drossing or molten metal extraction or fused salt extraction technique and results in only partial decontamination. Fluoride volatility processes appear to be especially favorable for recovery of enriched U and decontamination factors of 10/sup 7/ to 10/sup 8/ would be achieved by simpler means than those employed in solvent extraction. Data from lab research on the BrF/sub 3/ process and the ClF/sub 3/ process are given and discussed and pilot plant experience is described, all in connection with natural U or slightly enriched U processing. Fluoride volatility processes for enriched or high alloy fuels are described step by step. The economic and engineering considerations of both types of nonaqueous processing are treated separately and as fully as present knowledge allows. A comprehensive review of the chemistry of pyrometallurgical processes is included. Engineering and Economics is the title of book three which is concerned with several phases of chemical reprocessing of fuels which are of a general nature. Hot labs, radiochemical analytic al facilities, and high level development cells are described. Dissolution equipment, contactors, flow generation, measurement, and control equipment, samplers, connectors, carriers, valves, filters, and hydroclones are described and discussed. Papers are included on: radiation safety, chemical safety, radiochemic al plant operating experience in the U. S., and heavy element isotopic buildup. The general economics of solvent extraction processing is discussed, and capital and operating costs for several U. S. plants given. The Atomic Energy Commission's chemic al processing programs and administration are evaluated and the services offered and charges therefor are listed. (T.R.H.)
Descriptors: ALUMINUM ALLOYS; BROMINE FLUORIDES; CHEMICAL REACTIONS;

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Subject Codes (NSA): CHEMISTRY

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3. S. G. Thomson
4. F. F. Kaehland
5. J. R. Dem
6. K. M. Kraus

45-12-30

Compound of Hg^{++} and Pu (VI) - $Hg\ Pu\ O_2\ (CO_3)_2$ (?)

I. Identifications: INV. 65

The addition of Pu (VI) nitrate solution to a slurry of basic mercuric carbonate in 45% $K_2\ CO_3$ results in the formation of a green precipitate.(1)(2) Since Pu (VI) alone is soluble in the carbonate solution and since the basic mercuric carbonate is orange, a double salt of mercuric and plutonium has been suggested.(1)(2) Analysis of several precipitates indicate a Hg^{++}/Pu ratio of ca. one, the plutonium being present entirely as Pu (VI).(1)(2)(3) A possible formula may be $Hg\ Pu\ O_2\ (CO_3)_2$ by analogy to metal carbonate compounds formed with uranyl of the type $Ag_4\ UO_2\ (CO_3)_3$.(3)(2)

II. Color-Green.

III. Preparation.

The green precipitate was prepared either by adding $Hg\ (NO_3)_2$ to a solution of Pu (VI) in 45% $K_2\ CO_3$ or by adding Pu (VI) nitrate solutions to slurries of basic mercuric carbonate in the potassium carbonate solutions. In either case, the resulting slurry was agitated for four hours at 25°C. The orange basic mercuric carbonate precipitate was converted to a green precipitate within one-half hour. The precipitate was washed with potassium carbonate solutions and then analyzed for mercury and Pu. When only half as many moles of plutonium as moles of mercury were added to the slurry, the final green precipitate gave mercury to plutonium ratios of 1.2 and 1.1 in duplicate runs.(1) When one plutonium mole was added per mole of mercury, the ratios in quadruplicate runs were 1.28, 1.22, 0.82 and 0.80.(2)

In some cases a layer of the orange basic mercuric carbonate was noticed after centrifuging the ppt's. It was necessary in these cases to separate the green plutonyl-mercuric compound from the basic mercuric by mechanical means.

IV. Reactions -

Hydrolysis occurs on washing the green precipitate with water resulting in the formation of a white precipitate and a solution having the characteristic green color of Pu (VI)in K_2CO_3)/ Dissolving the washed precipitate (ca/mg Pu) in hydrochloric acid and diluting to 0.8 N-Hcl evolved CO_2 and gave a solution of 100% Pu (I) as determined by spectrophotometric analysis.(3)

V. Crystal Structure -

The X-ray deffraction patterns from one of these preparations which had been washed once with 45% K_2CO_3 were very messy and consisted chiefly of an unknown phase or phases.(5)

VI. Solubility -

After seven days in 45% K_2CO_3 at 25°C with approximately half as many Pu atoms as Hg atoms, solubilities of 0.38 and 0.29 gm of Pu per liter were obtained in duplicate experiments.(3)

(1) J. R. Dam and D. E. Koshland, Jr. , CL-P-354, (November 18, 1944)
(2) J. R. Dam and D. E. Koshland, Jr. , CL-P-368, (December 6, 1944)
(3) J. R. Dam and D. E. Koshland, Jr. , unpublished.
(4) Mellor, Volume 12, pp112-116.
(5) W. H. Zachariasen, MUC-FWHZ-106 (February 9, 1945)

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merc solvent alloy

OREX Summary Report Aug 52 • 52-9-97

OREX Summary for the Week Aug 52 • 52-8-188 Sept 52 Nov 52-12-41

? NO's of Hg Cells to Look at (analytical)

ALLOY ADP

OREX Bi-weekly Report Dec 52 • 53-1-106 • 52-10-192

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Orex Names

R.E. Blanco

F.L. Steely

N.L Carter

C.B. Baker

F.L. Culler

H.O. Weeren Y-12

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benzene "dries" the 90% PDA in water

03/14/96

These items have been provided to the searchers and have been approved for release to the public. Susan Flack requested the documents on the date given and their status is complete and delivered.

The following documents were requested on 3/01/96:

✓ CF-52-4-167	Notes on Orex Process
CF-53-1-320	Orex Planning Committee Meeting, January 22, 1953
✓ CF-53-10-177	Orex Test Facility Operating Manual
✓ CF-53-12-36	Review of the Purpose and Status of the Orex Development Program as of December 7, 1953
✓ CF-54-8-50	Termination of the Orex Project
✓ CF-54-8-244	Metallex Process, Flowsheet No. 2, Preliminary Cost Study
✓ CF-55-1-53	Status of the Metallex Process
✓ CF-55-1-79	Proposal for a New Program, Metallex
✓ CF-57-2-55	Metallex Objectives
CF-56-8-200	A Proposed Fuel Element Design to Facilitate Reprocessing by the Hermex Method
✓ CF-57-10-28	The Preparation of Thorium Metal by Sodium Amalgam Reduction of Thorium Chloride: The Metallex Process

Susan,

These 13 documents were requested by Young Moon to be sent to

Yankee Chem. Report Div. 1950-94

Teresa

Susan,

Enclosed are the 11 documents you requested.

Teresa

ORF File LIC Hearing

3420-0507 ~~44920~~ incl. blue [illegible] 120 34 RC

Document Griffith - Culler, F L

52-4-167 ✓ Notes on OREX Process

52-5-8 ✓ Survey of Problems Associated with OREX (Draft 1)

52-6-20 ✓ 14th Cost for Pilot Cleaner ... [illegible] ...

52-6-77 ✓ Guesstimate of Isotopic Analysis [illegible]

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52-7-140 ✓ Outline of Prelim Cost Study for OREX

52-8-47 ✓ Status Rpt for week end 8/1/52

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L. P. Twichell

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Weenfeng

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OREX

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9202	4-53 to 5-54	pilot plant
ANL 4501	4-54 to 11-54 (several months of	pilot plant component development
ANL 3592		

[redacted]

T. D.
SEP 2 1971
Bms

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From: W. L. Carter, H. O. Weeren, F. L. Culler

Subject: Notes on Orex Processes

[redacted]

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1.0 Introduction

This report is a summary of discussions held between the Materials Chemistry Division, Chemical Technology Division, and the K-25 isotope Separations Evaluation Group held during the month of March, 1952, particularly those from March 28 to April 1, 1952. The purpose of these meetings was to provide members of the Chemical Technology Division with information concerning processes for the separation of the isotopes of lithium. It should be pointed out that much of the information summarized herein came from meetings beginning on March 28, 1952, other data obtained from previous meetings and from lectures by John Shacter , K-25, have also been included in an effort to present all information now available that is pertinent to the Orex processes.

1.1 Purpose of Processes

The metallic element lithium as it occurs in nature is composed of the isotopes Li^6 - 7.2% and Li^7 - 92.8%. The Atomic Energy Commission is interested in obtaining large quantities of the light isotope Li^6 in enrichments of 95% or better.

The Materials Chemistry Division has investigated by literature search, laboratory, and pilot plant studies possible processes for the required isotopic separation. Reports of their work are available and are listed in the bibliography. From their work it has been concluded that chemical exchange processes offer the greatest possibility of success for separating Li^6 and Li^7. Systems using exchange reactions between the mercury amalgam of lithium and and salt solutions of lithium in both aqueous and slightly polar organic solvents have been developed on a laboratory and pilot plant scale as being the most promising. The exchange processes that now appear to be most promising are discussed in the following sections.

1.11 The "Elex" Process

The "Elex" process is based on the following exchange reaction:

$$Li^7(Hg) + Li^6(OH)_x \rightleftharpoons Li^6(Hg) + Li^7(OH)_x$$

in which the overall reaction constant is approximately equal to 1.05 (or the $\alpha = 1.05$). Aqueous solution of Li OH is contacted with a lithium amalgam with a back voltage applied across the interface between the phases to prevent the reaction of Li^0 in the amalgam with the aqueous Li OH solution. Enrichment of Li^6 occurs in the amalgam phase; a large cascade of contactors is required to enrich the Li^6 from 7.2 to 95%. In this system the amalgam phase is made cathodic and the aqueous phase anodic. Contactors used long trays containing

laboratory mixers every four inches. The interface must not be penetrated by a metal of low hydrogen overvoltage and must be maintained free of substances that reduce the hydrogen overvoltage of a mercury surface. Reflux of the streams is accomplished by electolytic procedures. It is essential that the concentractions of Li in both phases be kept constant throughout the cascade.

Because of the urgency for obtaining quantities of enhanced Li^6 the Elex process is being installed using 4" wide x 20' long trays in parallel to obtain necessary plant capacity and in series to obtain necessary cascade length. The cascade will be tapered with refluxers at every taper point. The Y-12 Engineering Department and the Vitro Corporation is doing design. Construction will be in Y-12 and the estimated cost is approximately $35,000,000.

The Chemical Technology Division will not engage in work on the Elex process.

1.12 The "Relex" Process

The "Relex" process is a proposal for an improved "Elex" process. It is based on the same fundamentals as the "Elex" process but would employ a more efficient contactor which would use deeper phase depths and agitation in a plane perpendicular to the direction of the desired gradient in the Li^6 - Li^7 separation. The "Elex" process provides agitation that is essentially parallel to the flow and hence produces greater stage lengths than if perpendicular agitation were used. The "Relex" process involves only a redesign of the contactor to increase plant capacity and decrease stage length.

No extensive work has been done on the Relex process. John Shacter's group has calculated approximate process advantages, but little development work has been done because of limitations of manpower and the urgency for a producing lithium plant. The Materials Chemistry Division is planning to test an improved contactor or contactors.

It is probable that the Chemical Technology Division will do little work on the Relex process; however, it may be desirable to expend some design and development effort on a better contactor.

1.13 The Orex Processes - Chemical Reflux and Dual Temperature

The Orex processes utilize the following chemical exchange reaction:

$$* \quad Li^6 Cl_{EDA} + Li^7 (Hg) \rightleftharpoons Li^6 (Hg) + Li^7 Cl_{EDA}$$

in which the overall reaction constant is approximately 1.051 at 26°C and

*Other solutes may have advantage. Reported in ORNL 1238.

decreases with increasing temperature. In this system Li Cl is dissolved in the polar solvent ethylenediamine (EDA) and contacted in a standard liquid-liquid extraction tower (pulse column under consideration) for sufficient stages to give highly enriched Li^6 in the amalgam phase. EDA (dry) will not react with the lithium amalgam phase, so that no applied potential is required to prevent the back reaction that occurs in the aqueous - amalgam system used for Elex. The two phases can be passed countercurrent in a pulse column of reasonable size. A cascade using the Orex processes would probably be tapered at several points. Reflux of the streams, which must be done at both top and bottom as well as at all taper breaks, can be accomplished in two ways:

1. Chemical reflux

   a. EDA - LiCl stream - evaporation to remove EDA from LiCl, "drying" LiCl from occluded and "hydrated" EDA, dissolution of LiCl in water and electrolyzed with Hg to make Li(Hg). There are other methods.

   b. Li Hg stream - contact Li (Hg) with EDA containing Na Cl in rock salt packed tower; Na replaces Li and EDA-LiCl feed to cascade; Na Hg reacts in a decomposer to produce Hg, Na OH. Hg then fed to Li(Hg) amalgamaker at bottom of plant. There are other methods.

2. Dual temperature reflux

   As previously noted the separation factor, α, varies with temperature in the EDA - amalgam system. At 26°C the α is approximately 1.055 while at 99°C the α is only approximately 1.028. By running a hot and cold column pair it is possible to obtain the reflux necessary in the separations cascade. The effective α of a hot-cold column pair is approximately 1.01.

Thus, the Orex processes employ the same chemical systems LiCl in EDA contacted with LiHg, but differ in the manner in which reflux is accomplished. The chemical reflux plant offers a higher overall α, but presents costly reflux operations. The dual temperature process offers a lower overall α, but presents rather simple reflux conditions.

It is proposed that the Chemical Technology Division assist in the investigation of the Orex process, reflux and dual temp, by building and operating pilot plants for each process. It will be necessary to do equipment development, lab investigations, and design work at ORNL. It is also proposed that ORNL undertake in conjunction with the Materials Chemistry Division and K-25, a preliminary economic evaluation of the Orex processes, and probably a preliminary design of the optimum process at full plant level.

To provide some orientation as to the comparative merits of each of the foregoing processes, John Shacter et al, have made preliminary economic studies. A summary of this work is reproduced below. It should be noted that these studies were made several months ago on the basis of very preliminary data and on guesses where data did not exist. The information is therefore not highly accurate and should be used only as a yardstick by which to measure the economic incentive for Orex process studies. No study has been made of the chemical reflux process since there were insufficient data at the time of the study. See Appendix I.- Proximate comparison of Elex, Relex A, Relex B, and Dual Temperature Processes.

1.2 Summary of Present Status of Work on Each Process

The following discussion is a very general summation of the writers' estimate of the present state of development of each of the processes discussed. It is not meant as a status report, nor does it in any way imply criticism; rather it has been included to provide personnel new to the project with a general perspective as to what must yet be done.

1.21 The Elex Process

a. Basic Chemical Data

The basic chemical data for the Elex process is rather well developed. Problems of crud formation, corrosion, control, analysis still remain. Basic solution properties are well developed.

b. Laboratory Scale Experimentation

Lab experiments conducted and reported by Materials Chemistry Division. Sufficient lab data have been accumulated for the construction and operation of a pilot plant and for design and initial construction of a full scale plant.

c. Equipment Development

Trays and agitators developed and are frozen for final plant design. Some equipment development proceding in pilot plant. All equipment for Elex process essentially frozen.

d. Pilot Plant Scale

Pilot plant in full scale, continuous operation.

1.21 (Continued)

e. Plant Scale

Plant now being designed by Y-12 Engineering Department, Materials Chemistry Division, Vitro Corporation (as Architect-Engineer), and K-25 Production Division.

f. Organizations Involved

1. Basic data - Materials Chemistry Division
2. Lab development - Materials Chemistry Division
3. Pilot plant - Materials Chemistry Division
4. Equipment development - Materials Chemistry Division
   - Y-12 Engineering
   - Vitro Corp.
5. Plant design
   - Production Division - K-25
   - Materials Chemistry Division
   - Y-12 Engineering Dept.
   - Vitro Corporation

1.22 The Relex Process

The revised Elex process will utilize most of the basic data developed for the Elex process. The difference in the Elex and Relex is in the type of contactor and method of phase agitation. Both the Materials Chemistry Division and John Shacter's group and K-25 have considered revisions for contactors; some plant scale scouting calculations have been made. Very little equipment development and essentially no pilot plant work has been done.

1.23 The Chemical Reflux Process - Orex

a. Basic Chemical Data & Laboratory Scale Experiments

Basic chemical data is now being obtained by the Materials Chemistry Division. A proposed and feasible flowsheet has been prepared although many alternates to various steps in the process have not been thoroughly studied. These are sufficient data, probably, to proceed with pilot plant design. See Section 3.0 for detailed data summary.

b. Equipment Development

The only equipment studied in any detail has been the pulse column contactor and this to a limited extent. Sufficient data are available on the contactors from the dual temp work to make design of contactors possible.

1.23 b. (continued)

The reflux systems will require unit equipment development, preferably before pilot plant design is frozen. Other process auxiliaries are in the same status. An 0.43" pulse column for CR process testing has been constructed and operated for several weeks by the Materials Chemistry Div.

c. Pilot Plant Scale

No pilot plant scale work has been done. It is proposed that the Chemical Technology Division do this work, with assistance and data from all other interested groups.

d. Plant Scale

No plant scale studies have been made. Preliminary proximate plant studies using existing chemistry and proposed equipment should be made as early as possible. After pilot plant has been operated, detailed studies and preliminary design is required.

e. Organizations Involved

1.	Basic data	- Materials Chemistry Division - Chemical Technology Division (possibly)
2.	Laboratory development	- Materials Chemistry Division - Chemical Technology Division
3.	Equipment development	- Materials Chemistry Division - Chemical Technology Division
4.	Pilot Plant	- Chemical Technology Division - Materials Chemistry Division - K-25 Production (Shacter)
5.	Plant Scale	- Chemical Technology Division - Materials Chemistry Division - K-25 Production (Shacter)

1.24 The Dual - Temp Process

The dual temperature process is slightly more advanced than the chemical reflux process but most of the comments made on the chemical reflux process apply with the following exceptions.

1. A dual temperature column set has been successfully operated by the Materials Chemistry Division. As a consequence more data are available than for the chemical reflux.

1.24 (Continued)

2. A preliminary economic study (2 months old) has been made by Shacter's group. A new study should be made at the time chemical reflux process is studied by the Chemical Technology Division.

2.0 Notes on ADP and Orex Organization

The ADP Steering Committee is:

C. E. Larson
F. L. Steahly
G. H. Clewett

To coordinate the planning and prosecution of the Orex phase of the ADP program a Planning Committee has been formed:

J. W. Ramsey - Materials Chemistry Division (Y-12)
H. M. McLeod - Materials Chemistry Division (Y-12)
W. M. Johnson - Calculations Section (K-25)
T. A. Arehart - Unit Operations Section, Chemical Technology Division (X-10)
R. E. Blanco - Laboratory Section, Chemical Technology Division (X-10)
R. B. Lindauer - Pilot Plant Section, Chemical Technology Division (X-10)
W. L. Carter - Design Section, Chemical Technology Division (X-10)
H. H. Garretson - Materials Chemistry Division (Y-12)

This committee holds regular weekly meetings at Y-12, on Friday at 10:00 AM. The chairmanship of the committee rotates through the group, depending upon the location of most active work load in the various sections. Any personnel working on the project other than the regular committee are invited to attend all meetings. J. W. Ramsey has been serving as chairman and secretary.

The planning committee is responsible for overall coordination and administration of the Orex project. In each meeting the results of work in progress are reviewed and plans made for future work. As the project progresses, the committee will make all necessary decisions regarding process and job planning, or in cases where decisions cannot be made by the committee, to refer problems to section chiefs or to the Steering Committee for resolution. The Planning Committee thus serves two purposes: to provide constant laison between all groups and to provide coordination and decisive action during the progress of the job.

[redacted]

3.0 Data on the Orex Processes

On March 25, and March 28, 1952, meetings were held to discuss in detail the two Orex processes, chemical reflux and dual temperature, to be referred to hereafter as CR and DT respectively. The purpose of these meetings was to provide the Chemical Technology Division with all existing process data and calculations as developed by the Materials Chemistry Division and other groups. These data are to be used to design, construct, and operate a pilot plant for both the CR and the DT processes at X-10 and to outline supporting laboratory and equipment development problems.

It is hoped that these pilot plants can be constructed by September, 1952, and ready for operation in January 1953. At present it is proposed that the development facilities be constructed in the empty cell bay on the west side of Building 4501 in X-10.

At present, the Orex program has three main objectives:

1. Study, on the basis of existing process knowledge, the capital and operating costs at full plant level for both the CR and the DT processes. It is understood that such a study will be of value only as a preliminary analysis, since exact engineering data will be unavailable. This study will be done in conjunction with John Shacter, et al, at K-25 and based on data supplied by the Materials Chemistry Division.

2. Develop, design, and operate pilot plants for both the CR and the DT processes. This will entail laboratory and equipment development. At the conclusion of the pilot plant program, sufficient chemical and engineering data should be available for a second economic study which should lead to the selection of the best ADP process and to the determination of optimum plant size.

3. Economic studies leading to selection of optimum process and optimum plant size followed by preliminary design of a production scale plant in sufficient detail to be used by an architect-engineer. It is hoped that this phase of the work can be completed by July, 1953.

The following sections present detailed discussions of the Orex processes. Each process step is discussed and an attempt has been made to list the information required from each piece of equipment during pilot plant operation.

3.1 The Chemical Reflux Process - Summary Pilot Plant Discussion

[redacted]

3.11 Proposed Pilot Plant Size

Capacity: 0.1 lb Li^6 per day

Enrichment: 95% Li^6

Probable column sizes: Three - 3" columns x 34' high

Feed: Amalgam phase of natural Li containing 92.8% Li^7 and 7.2% Li^6.

Bottoms: 95% Li^7

Preliminary calculations: Appendix II. (From G. H. Clewett) for Pilot plant

Preliminary plant scale flow diagram: Appendix III. Figure 3 (from Materials Chemistry Division

Schematic pilot plant flowsheet: Figure 1. Amalgam - Amine Chemical Reflux System.

3.12 Objectives for Pilot Plant

The data and information expected from the pilot plant was discussed at length to establish general plant requirements. The following is a summary of notes taken on March 25, 1952, concerning purpose of pilot plant.

1. Demonstrate the overall operability and chemistry of the EDA-Amalgam system as shown in flowsheets, and obtain cost experience in operation.
2. Collect capital cost data.
3. Develop equipment satisfactory for plant scale operation.
4. Prove instrumentation, pumps, controls.
5. Provide necessary data for scale up to plant scale.

3.13 Basic Data on CR System

The following basic process information has been compiled from meeting minutes and reports provided by the Materials Chemistry Division. It is recorded in a somewhat random fashion.

[redacted]

1. Properties of ethylenediamine - $NH_2\ CH_2\ CH_2\ NH_2$

Density: .963 21/4 gm/ml. (hydrate, MW: 78.12)
.899 20/4 gm/ml. (dry. MW: 60.10)

Boiling point: 118°C hydrate
116:1-117°C anhydrous

Temperature stability: Stable to at least 180°C. Possibly decomposes at 130°C in contact with Li(Hg)

Specific heat: .84 BTU/# °F for dry EDA

Maximum boiling mixture with water: BP = 118.5°C, 83% EDA, 17% H_2O

Viscosity: 0.0261 poise @ 0°C
0.0126 poise @ 25°C
0.0074 poise @ 50°C

Cost: Present: 99.5% $1.00/lb
76% $ .47/lb

Supplier: Carbide and Carbon Chemicals

Flash point: 93°F open cup, dangerous fire hazard (CF 52-4-46)

Explosive limits: Not yet determined

Toxicity: Vapor and liquid dangerous to eyes. (CF 52-4-46). Caustic Reaction. Some dermititus.

Vapor pressure vs. temperature: (Perry, Chemical Engineers Handbook, 3rd Edition, 1950, page 159

T°C	p (mm Hg)
30	18
50	52
70	120
90	240
100	440
110	620

(This is for a 20% water mixture)

[redacted]

1. (continued)

Density of vapors: Heavier than air

Conductivity (electrical): Poor-hazard for static electricity

Thermal Conductivity: 0.00067 cal/sec cm^3 (Weber's equ.)

Process requirement: EDA anhydrous to better than 99.5%. Prepared by distilling from pot containing CaC_2 or sodium and tested by checking blue coloration of freshly cut sodium in EDA. If 99.5% bought from Carbide, EDA must be redistilled over CaC_2 or Na, preferably CaC_2.

Purity: Not yet specified

Heat of vaporization at B.P.: 11,200 cal/mol

Heat of fusion at M.P.: 4,610 cal/mol

Melting point: 110°C (also given at 8.5°C)

Dielectric constant at 18°C : 16

Additional solubility and conductance data given in references in the bibliography at the end of this report.

[redacted]

2. Properties of Mercury

Density: 13.546 Mol wgt: 200.61

Specific heat: 25°C - .03320 (Chem. Rubber - p 1796)
100°C - .03269

Viscosity: 20°C - 1.55 centipoise
100°C - 1.24 centipoise

Cost: $210-214/76 lbs.

Suppliers: Many

Toxicity: See CF 52-4-46. Toxic limit: 0.1 mg per cubic meter of air. Very serious poison.

Conductivity (electrical): 95.78 microhm - centimeters @ 20°C

Conductivity (thermal): 17°C 0.0189 cal/cm/°C
50°C 0.0197 cal/cm/°C

Process requirement: Absolute pure Hg. Must be dry. After amalgamakers, LiHg must be stored under dry helium atmosphere.

Vapor pressure:

Temp °F	mm Hg	mg Hg/cu. meter air
0	0.000023	0.3
32	0.000185	2.2
50	0.000490	5.6
60	0.000816	8.7
70	0.00131	14.0
80	0.00212	22.0
90	0.00326	35.0
100	0.00507	53.0

Coefficient of thermal expansion: 41×10^{-6}

[redacted]

[redacted]

3. Properties of Lithium Chloride - LiCl

Molecular Weight: 42.40

Density (dry): 2.068 - 25°C

Density (hydrated) LiCl · H_2O: 1.78

Molecular weight (hydrated) : 60.41

Solubility in EDA (anhydrous) (From ORNL 1238):

Temp. °C	mols/liter
12.5	0.1486
20	0.2020
29	0.3113
45	0.6570
60	1.369
77	2.584
96	4.741
25-27°C	0.32

Also see plot ORNL 1238, page 37.
LiCl slowly soluble in EDA (anhydrous)

Solubility of Lithium Chloride in H_2O: (Chem. Rubber)

Temp °C	gms/100 gms water
0	67
20	78.5
40	90.5
60	103.0
80	115.0
100	127.5

Note: Physical property data on LiCl solutions necessary

Assume that reflux plant concentration will be .2M LiCl in EDA. This may be changed since it may be more economical to operate columns at temperatures higher than room temperature.

[redacted]

4. Properties of Lithium Amalgam

Solubility of Li in Hg: (data available from 0 to 80°C)

Saturation at 25°C: 0.92 M (gm atoms/liter of Hg)
Saturation at 60°C: approximately 1.5M

Activity of Li in Hg is well established from 15°-55°C. (These data may be obtained from Garretson, Y-12)

Garretson says that literature records Li(Hg) as stable in dry, CO_2 free air. He expresses opinion that it will not react with N_2 when dry. The reaction of Li(Hg) with N_2 is being checked in lab at Y-12.

Assume that amalgam used in reflux process is 0.5M Li in Hg. (gm mols/liter). Ramsey has operated columns using 0.75 M Li(Hg).

Lithium amalgam reacts slowly with water if Cr, V, Fe not present.

5. Properties of LiOH and LiOH water solution

Reference: ORNL 1254, p 51 for purification procedures if required. Commercial LiOH may not be satisfactory as feed plant through amalgamaker since impurities transfer to amalgam and may concentrate in cascade.

6. Solubility of NaCl in EDA

25°C	0.05 M approx.
100°C	0.02 M approx.

7. Temperature of Operation of Pulse Column Cascade

Temperature of operation for the pilot plant should be assumed to be 26°C. This may be changed to take advantage of higher LiCl solubility in EDA at the expense of the separation factor α. The pilot plant columns should be designed for temperature control and should be provided with a heating system to raise the column temperature to at least 60°C, where the solubility of LiCl is 1.37/.25 = 5.5 times while the α is reduced from 1.051 to 1.041, approximately. Accuracy of temperature control should be specified.

8. Separation Factor of EDA-LiCl-LiHg System (From ORNL 1238)

Temperature °C	α
26° ± 1°C	1.048 ± .002 (amalgam) 1.051 ± .013 (EDA)
60°C	1.041 approximately
99°C ± 1°C	use 1.028 ± 0.010

[redacted]

3.14 Detailed Description and Data for Major Process Units - See Figure 1

The following sections summarize discussions on each major process unit. Alternate methods are discussed. To simplify the discussion it has been assumed that the process shown in Figure 1 is to be installed and that other methods are possible alternates to be evaluated before possible inclusion in the flowsheet.

1. The Pulse Column (columns, because of height restriction and desirability of plant taper)

The contactor selected for the reflux process has been a pulse column in which the amalgam phase is passed countercurrent with the EDA-LiCl phase. The amalgam phase is enriched with Li^6 as it passes down (up in terms of enrichment) through the pulse column cascade.

Reflux of both streams is required at the bottom of the stripping section, at each taper point, and at the top of the cascade. Methods of reflux are covered in subsequent sections.

Pulse column data from Y-12 DT pilot plant studies to date are summarized below:

a. HTU (HETS) 6" ± 2" use 8"

b. Flooding rates: (at room temp. ~ 26°C)

30 mesh ss screen @ 100°C	3610 gph/ft^2	amine
24 mesh ss screen @ 24°C	760 gph/ft^2	amal.
	4370 gph/ft^2	total
20 mesh ss screen @ 100°C	4180 gph/ft^2	amine
10 mesh ss screen @ 24°C	1064 gph/ft^2	amal.
	5244 gph/ft^2	total

These data were collected in a 1" OD X 16 gage type 316 ss column.

Use flood rate of 4000 gal/hr/ft^2 for calculation, which should be approx. 80% of flooding.

c. Pulse amplitude and frequency have not been well defined by data. Some data are available from Y-12 DT pilot plant reports.

d. Experimental work to date has been done on columns with plates 1" apart and made of stainless steel screen of mesh sizes varying from 60 mesh down to 10 mesh. Ramsey (ORNL-1238) points out that nickel plates or screens may offer an advantage because of preferential wetting by amalgam.

e. Feed streams to Ramsey's columns contain sintered stainless steel filters of 20 micron pore size on both the amine and amalgam phases.

f. Material of Construction:

Column and Plates: Type 316 s.s. used and probably OK but corrosion studies of welds should be made. Type 302 and possibly 303 may not be good because of fitting tendencies in slightly alkaline chloride solutions. Pilot plant better in Type 316.

Piping - stainless steel, preferably Type 316, but Type 304 is probably satisfactory for Pilot Plant. Tubing and tubing fittings should be used almost exclusively. Flanges and threaded joints should be kept to a minimum.

Packing and gaskets - lithium amalgam reacts with all gasket materials except asbestos (ORNL-1238, p 27). EDA reacts with all except teflon and asbestos. Ramsey has used Garlock No. 7735 sheet. Pump packing has been chevron type blue african asbestos.

Pipe dope - Cyl-seal, West Chester Chemical Company, West Chester, Pa.

g. Pumps and pulsers - Must be decided. Ramsey has used Milton Roys but recommends something better. Pumps coupled with instrumentation must provide very close column control in order to keep the mol ratio of lithium in the two phases constant. The accuracy and precision of the control system has not been determined, but it should be approximately 2%.

h. Instrumentation - not developed. Interface, stream flow, and concentration measuring and controlling instruments must be developed.

i. Sealing - the entire cascade must either be completely sealed, or the system maintained under an atmosphere of dry helium. All valves and pumps must be leak proof or blanketed at possible openings with helium.

j. Temperature - Column and possibly column auxiliaries must be temperature controlled. For purposes of design assume that column will operate at 26°C but that it will be necessary to raise temperature to approximately 60°C.

During pilot plant operation, and possibly in supporting preliminary equipment studies, the following information should be determined:

a. Optimum operating temperature
b. Separation factor
c. Accuracy of ratio control system
d. Optimum packing spacing and hole size
e. Flooding data in sufficient quantity to do scale-up.
f. Stage heights
g. Pulsing frequency and amplitude
h. Column equilibrium time
i. Residence time for each phase in system
j. Optimum volume and mol ratio of phases
k. Operating costs
l. Capital costs
m. Variation of all variables with reflux rate
n. Desirable % flooding for operation.

In the pilot plant, approximately 250 stages or less will be required. At the proposed flows it is probable that columns not larger than 3" in diameter will be required. Each column will be between 30 and 40 feet tall; one column will serve as the stripping section, while the other two will be enrichers. It is conceivable that the pilot plant could be built advantageously without a taper.

Alternate contactors can be considered as an equipment study. Possible alternates are packed columns and the podbielniak centrifugal extractor.

2. Lithium hydroxide electrolyzer - amalgamaker

The lithium hydroxide electrolyzer will produce feed amalgam for the pilot plant and is therefore of small capacity, equaling about product rate plus losses in the pilot plant. The tray electrolyzers developed and available for the Elex process should be useful in the CR Pilot Plant. Amalgam feed for both the CR and the DT can be made in the same electrolyzer.

Amalgam make-up is discussed in reports ORNL-1254 and ORNL-1238. The Mathieson Chemical Company is doing development work on plant scale amalgamakers. The feed amalgam is prepared by the electrolysis of natural lithium hydroxide. In the feed preparation approximately 3.5 M LiOH (92.8% Li^7 and 7.2% Li^6) will be fed to the electrolytic cell. Lithium and hydrogen ions will migrate to the mercury cathode where hydrogen will be evolved as a gas and lithium will go into solution in the mercury to form the amalgam. Oxygen ions will migrate to the anode and be evolved as a gas.

Purity requirements for the lithium hydroxide feed to the amalgamaker have not been established. In the Elex process as reported in ORNL 1254, it is necessary to maintain high purity in the LiOH which is fed directly to the cascade, but these purity specifications may not be required in the Orex processes if the impurities which transfer along with lithium to the amalgam do not build up in the cascade.

At present, there seems to be no justification to investigate on a pilot plant scale any other type of feed amalgamaker. However, in the final plant, it may be desirable to use an amalgamaker of different design as developed by Mathieson.

3. Product Decomposer

A portion of the product stream of lithium-mercury amalgam of 95% Li^6 enrichment is bled off and sent to a contactor where the isotope is separated from mercury. This is accomplished by passing the amalgam countercurrent to water over the surface of an iron impregnated graphite catalyst. The iron graphite furnishes the active surface for shortcircuiting the cell set up between the amalgam and aqueous phases causing the lithium to go into solution in the water. Hydrogen is released in this reaction, and enriched Li^6OH is obtained as product. The mercury stream from the contactor is returned to the electrolyzers for the production of more amalgam.

The units used in the pilot plant for Orex can be similar to those used in the Elex pilot plant. Drawings for these units are available from McLeod in Y-12.

The graphite catalyst is prepared by impregnating C-18, AGOT-3, or AGHT (National Carbon Co.) graphite with an iron solution and then sintering at 1000°C. Exact flow conditions and arrangements must be determined.

The design and development of this unit is being carried out by Mathieson Chemical Corporation. The laboratory probably will be concerned only with the problems of disposing of hydrogen off-gas and determining the life of the graphite catalyst, which is now unknown. Catalyst in the Elex pilot plant has been used for more than two months without apparent deterioration.

As an alternate to the amalgam decomposition, it is possible to draw off the EDA-LiCl stream and evaporate. At some point during the development program this alternate should be studied from an economic standpoint.

4. The Li^7 Reflux System

The Li^7 reflux system consists of an EDA-LiCl salting evaporator, EDA condenser, a LiCl crystallizer, a centrifuge, and a LiCl dryer (possibly using benzene as shown on Figure 1). In addition an EDA-benzene distillation tower (and EDA drying system) is also part of the completed cycle. If the pilot plant, as now conceived, consists of one stripping column plus two enriching columns and if the stripping column is of the same diameter as the largest enriching column, no refluxer will be required between the enricher and the stripper.

Alternate reflux systems for Li^7 have been proposed and will be described under Alternate Li^7 Reflux Systems. For design purposes it will assumed that the evaporation - salting - amalgamaker system will be used.

Each process component for the evaporation system is discussed in the following sections.

a. The EDA-LiCl Salting Evaporator - Crystallizer Separator

McLeod has proposed that the EDA be evaporated in a standard salting type of evaporator in which approximately 90% or more of the EDA is boiled off. The evaporator concentrate can then be dumped to a crystallizer for LiCl recovery.

The evaporator should be a continuous unit with both continuous feed and salt draw-off. If continuous draw-off is not too feasible, batch draw-off could be used while still retaining continuous feed.

Mr. McLeod has proposed to run the evaporator under vacuum at 200 mm pressure at approximately 178°F. This vacuum system will complicate slightly the discharge of salts to the crystallizer unless it too is under vacuum. In any event, the continuous removal of the LiCl crystals - liquor to the centrifuge will require a set of dump-vacuum breaker tanks. The entire system must be maintained under dry helium, dry air or N_2 if satisfactory.

It was also proposed that spray drying following initial EDA boil-off be considered.

The foaming tendencies of the EDA lithium chloride solution have not been determined.

The following information should be collected in the pilot plant or in unit process studies before the evaporator is designed:

1) Foaming characteristics of EDA-LiCl system throughout concentration range at various pressures.

2) Optimum vacuum

3) Salting characteristics of solution; conditions for optimum crystal growth.

4) Settling and centrifuging characteristics of salt

5) Performance of filters on salt

6) Entrained lithium chloride in EDA overhead. Also establish separation required between EDA and LiCl

7) Heat transfer coefficients for heating and cooling

8) Scaling characteristics of solution

9) Optimum vapor velocities for maximum decontamination

At the present time there is very little information available on this phase of the process.

b. LiCl - Crystallizer

1) The type of crystallizer has not been discussed; no information either chemical or equipment is available. It is suggested that component work start on this unit. It will probably operate under a vacuum and be heated with steam. Standard crystallizer designs should be checked.

2) A spray drier using the evaporator heel as feed was suggested. Drying would preferably be accomplished by recirculated superheated EDA rather than with a heated gas such as helium, since such a gas would be noncondensible and would increase condenser size and EDA loss.

3) LiCl crystallizers along with two (possibly one) molecules of EDA. This EDA must be removed from the salt before it is admitted to the brine makeup system. Garretson indicated that he thought that it might be possible to crystallize LiCl without the EDA. Chemical development is needed on this phase of the process. It was the group's opinion that spray drying might provide an EDA free LiCl, but no experimental evidence exists.

4) R. E. Blanco suggested that it might be possible to use an almost saturated lithium chloride solution to dissolve and remove LiCl from EDA. Since concentrated LiCl solution is used as a drying agent in industrial air conditioners, it is possible that EDA-saturated LiCl might be immiscible. The lithium chloride could then be fed directly to the amalgamaker.

c. The Salt Separator - Centrifuge or Filter

Several types of separators can be considered:

1) Centrifuge - which must be air tight and leak-proof. No salt losses are permissable. Many "dewatering" centrifuges are made for totally sealed operation such as the Sharples Dehydrator, Bird Continuous Super Decanter, others. Centrifugation characteristics must be investigated.

2) Filters totally enclosed and continuous filters can be used. Oliver and other filters could be considered. For pilot plant work, a filter system may be desirable because of greater availability. Filtration characteristics must be determined before and during pilot plant operation.

3) No development information exists on this separation. It is desirable that almost all LiCl be recovered and the EDA stream be free of LiCl. For this reason, EDA streams from the crystallizer and separator should be returned to the evaporator for recycle.

d. The LiCl Dryer

LiCl salt will probably require drying with hot benzene vapor to remove the residual EDA. McLeod has proposed that this be done by blowing heated benzene vapor through a moving bed of LiCl crystals. The benzene - EDA vapor is sent to EDA - benzene still, while EDA free lithium chloride is discharged from the column after some heating to drive off benzene.

No development information exists on this step. Both chemical and equipment development are required. After EDA has been removed, the LiCl crystals can be handled in air.

e. The EDA Recovery and Recycle System

The EDA stream from the evaporator may be sufficiently dry and free of lithium chloride to be reused immediately for top reflux EDA-LiCl make-up.

It is probable, however, that the EDA will require drying which can be done by distilling EDA from a pot containing $CaCa_2$ or Na metal. Since it will be necessary to dry fresh EDA (make-up EDA) as purchased from the supplier, the same drying still can be used.

The EDA-benzene streams must be fractionated in a distillation tower. No data exists at present on this step, although Carbide and Carbon should be able to supply some information.

Benzene will be stored for reuse in the LiCl drying step. All equipment containing EDA should be absolutely moisture free and, consequently, air tight. Dry helium has been used as a blanket gas.

f. Lithium Chloride Brine System and Amalgamaker

The lithium chloride free from EDA and depleted in Li^6 is dissolved in water to the maximum concentration usable in the electrolysis cell. No development information is available on the brine requirements or on the electrolysis cell. Mathieson Chemical Co. is doing development work for the LiCl unit. The cell will be similar to a standard NaCl - NaOH cell. Mathieson should be contacted as soon as possible concerning a unit suitable for use in the reflux pilot plant. It should be noted that this unit will be the largest amalgamaker (or amalgamakers) in the reflux plant. Probably two LiCl amalgamakers will be required in the pilot plant if only one column size reduction is included.

In the reflux amalgamaker lithium chloride brine solution is fed to the electrolytic cell. As in the feed amalgamaker, the lithium ion migrates to the mercury cathode and forms the amalgam; at the anode chlorine gas is evolved.

Preliminary discussions concerning the operation of the amalgamakers indicate that data should be obtained in the pilot plant on operating techniques and variables as enumerated below:

1) Capacity, rate of amalgam production and power utilization.

2) Purity of amalgam from the standpoint of dryness

3) Volumes of hydrogen, oxygen and chlorine off-gases and their disposal

4) Maximum concentration of lithium in mercury that can be processed; temperature dependence

5) Cooling requirements of streams in amalgamaker

6) Purity of recycle mercury feed to amalgamakers; necessity of additional clean-up facilities

7) Explosion hazards of hydrogen and chlorine mixtures

8) Necessity for amalgam feed and amalgam reflux holdup tanks

9) Strength of LiCl brine solution to be maintained in amalgamaker. Efficiency of electrolysis decreases at low salt concentrations.

10) Operating and capital costs

Miscellaneous notes collected on the LiCl amalgamaker are summarized below:

1) It is possible, though not probable, that the mercury stream coming from the bottoms refluxers may have to be cleaned before use, but Clewett states that in a circulating system mercury obtained by decomposition of amalgam is immediately ready for use in amalgamakers without a major cleanup step.

2) After the amalgam has been prepared to a strength of approximately 0.5 to 0.75 M in helium (or higher), the amalgam must be dried, filtered, redried, then collected and stored under an atmosphere of dry hydrogen in a vessel previously flushed with dry hydrogen. In pilot plant work Ramsey has shown that decantation of fresh amalgam may be sufficient to provide dry amalgam feed.

3) It has been noted in ORNL 1238, p. 15, in the section on amalgam makeup, that approximately 60 to 70% of the LiCl in the brine phase transfers to the mercury. Therefore, a recirculating brine system should be installed to recycle spent brine to the brine makeup tank (s) to bring brine back to entrance concentration (as yet undetermined).

4) The concentration of the amalgam leaving the amalgamaker should be constantly checked by a continuous instrument controlling the amperage to the electrolysis cell. Allowable variations in amalgam concentration must be determined. This also requires that the brine concentrations be fairly constant so that the amalgamaker produces Li(Hg) of constant molarity.

5) Based on G. H. Clewett's preliminary calculations the amalgamaker (s) must produce approximately 25 gal per hour (94 liters) of 0.5 M LiHg.

6) It is probable that an amalgam feed tank at the stripper exit and the plant taper point will be required to serve as a built in surge capacity for the system.

7) Some means for checking the purity of the prepared Li(Hg)must be provided for the pilot plant. If possible a continuous system is desirable, since the reflux system may most economically be operated continuously.

8) Special sampling devices will be required to take samples which exclude moisture and air.

9) Pumps or other movers for all streams must be provided.

10) Material of construction for this system will probably be Type 316 stainless steel for the pilot plant. However, see a discussion of this point under 3.15.

g. EDA Preparation

It is essential that all EDA used in this process be absolutely dry. Moisture in the pulse column attacks lithium in the amalgam phase and precipitates LiOH. Also only very small quantities of water are necessary to remove all lithium from the amalgam. A commercial grade of EDA contains about 23% water by weight; however, this mixture can be supplied dried to 99.5% EDA by the vendor. The remaining 0.5% water, however, is very difficult to remove, and the price is correspondingly increased. Several schemes for drying EDA have been presented; these include drying over sodium, drying over calcium carbide and drying by distillation with benzene.

Some of the problems with which the laboratory will be concerned in the preparation of dry EDA are as follows:

1) Development of a satisfactory drying procedure

2) Development of proper storage facilities for dry EDA

3) Determination of the extent of dryness required for EDA

4) Determination of whether commercial EDA should be dried in the laboratory or whether EDA of the proper dryness should be bought from a vendor. Shipping bone dry EDA might be such a problem that it will be better to dry it at the laboratory

[redacted]

h. Alternate Li^7 Reflux Systems

1) There are possibilities for direct electrolysis of EDA-LiCl to make Li(Hg). No work has been done on this alternate. It was agreed that definative scouting work should be done.

2) Blanco suggested the possibility of using continuous ion exchange as a reflux method. Blanco will investigate.

3) The opinion was expressed that a reflux system which does require handling dry lithium chloride is desirable.

5. The Li^6 Reflux System

Li^6 must be refluxed in the amalgam phase at the taper point and at the top of the plant. The system now proposed for the Li^6 Hg reflux has not been too well tested on a laboratory scale. As shown in Figure 1, it consists of a contactor for Na Cl (rock salt), dry EDA containing 0.05 (at 20°C) Na Cl, and Li Hg. It was pointed out that the reflux on this end (the enriched end) of the cascade must be very efficient with no loss since losses here mean proportionate increases in both cascade length and width.

It is proposed that the Li(Hg) stream be contacted in a column packed with rock salt with EDA (from EDA evaporator) saturated with Na Cl. Flowing countercurrent to the amalgam phase over the Na Cl bed, the EDA stream picks up Li Cl formed as sodium replaced Li in the amalgam and carries it upward into the enriching section of the pulse column. The mercury phase, which becomes richer in sodium content, leaves the bottom of the inversion column and becomes the feed to the sodium-amalgam decomposer. The reaction occuring in the inverter can be shown as follows:

$$LiHg + NaCl + EDA \rightleftharpoons NaHg + LiCl_{EDA}$$

$$k = \sim 10^3$$

Preliminary thoughts concerning the operation of the NaCl - LiHg - EDA column indicate that experimental work should be directed along the following lines:

1. Determination of the efficiency of the LiHg - NaCl - EDA transfer

2. Feasibility of using a rock salt packed tower and passing LiHg and EDA countercurrently over same.

[redacted]

3. Feasibility of introducing NaCl as a slurry with EDA at bottom of column and operating the column as a slurry pulse column.

4. Optimum ratio of Na: Li.

5. Determination of NaCl - EDA - LiCl phase diagram

6. Determination of optimum operating temperature

7. Required purity and dryness of NaCl

Following the reflux tower where the Li^6Cl is transferred from the amalgam phase to the EDA phase, the NaHg amalgam must enter a decomposer. Here the NaHg is contacted with water and is identical in operation with the product decomposer described previously. Hydrogen gas is released in the decomposition of the amalgam; sodium hydroxide and mercury are obtained as the other streams. The mercury is returned to the amalgamakers, and the sodium hydroxide goes to waste.

The Mathieson Chemical Corporation is concerned with the design and development of this decomposer; the laboratory will probably be concerned only with the disposal of the off-gas, determining the life of the graphite catalyst and the effect of sodium carry over in the mercury feed to the amalgamakers.

The following sections summarize details of operation for the components in the Li^6 reflux. Alternate reflux systems are discussed under Alternate Li^6 Reflux Systems.

a. The NaCl - Li(Hg)- EDA (LiCl) Column

1) LiCl dissolves to about 0.25M in EDA at room temperature but NaCl is soluble only to the extent of 0.05 M at the same temperature. Therefore, to dissolve sufficient NaCl in the EDA stream to complete exchange with the Li in the LiHg, it is necessary to provide excess solid NaCl to be constantly dissolved as the exchange occurs. Lab tests of a packed rock salt column at Y-12 gave the following results:

Column diameter = 1" glass
Depth of salt (NaCl) = 10-1/2"
Flow rate Li(Hg): 7 cc/min
EDA at faster rate

Results: Li(Hg) stream leaving column contained approximately 25% of initial quantity of lithium.

2) The cell potential between Li(Hg) and NaHg is approximately 0.2 volts in favor of Na replacing Li.

3) No experiment has been performed that indicates that all the lithium can be replaced by sodium in this system. Garretson says that classical solubility laws should be followed since both Na and Li are completely ionized in EDA solution. However, it is necessary that a phase diagram for the Na Cl, LiCl, EDA system be developed as suggested by Shacter.. Since 100% transfer of the Li is required, the possible back-salting effects of LiCl going into the EDA phase must be exactly defined. Y-12 will develop this information.

4) Clewett pointed out the limitations that must occur at the top of the rock salt column. The quantity of sodium which goes up the cascade must be essentially zero, or at most the ratio of $\frac{Na}{Li}$ should not exceed $\left(\frac{V}{D}\right)_{actual}$ times 1000. This says that the amount of sodium entering the top stages of the cascade should be less than $\frac{1}{1000}$ of the product draw-off rate.

5) Culler suggests that a pulsed slurry column using EDA-NaCl slurry in contact with the Li(Hg) be tried. It was agreed that this problem would be investigated at X-10 as soon as possible, but that an attempt should be made to try it at Y-12 because of the lag time which will occur in setting up component systems at X-10.

6) No evaluation has been made as to the impurities in NaCl. Y-12 will attempt to define the effects of impurities.

b. The EDA Feed System

1) EDA feed for this refluxer will come from the Li^7 reflux system and must be dry and free of all low quality Li.

c. The NaHg Decomposer

1) Mathieson is developing this unit which contacts NaHg over an iron impregnated graphite catalyst previously described. Information on this unit must be obtained from Mathieson.

2) Commercial practice does not lead to the complete decomposition of NaHg to NaOH, Hg, and H_2. Commerical units now have streams running concurrent. It was suggested that countercurrent operation might yield complete decomposition.

3) For pilot plant work, units similar to those employed for Elex pilot plant work on Li(Hg) decomposition may be satisfactory.

4) Mercury leaving the decomposition system is used to make Li(Hg) in the Li^7 reflux and to prepare feed to the cascade. For this reason it must be completely free of Na. Possibly a second decomposer in series with the first may be required.

5) Mercury must be completely separated of aqueous phases from the decomposers to prevent carrying Na to the Li^7 reflux. This will require washing Hg with water.

d. Alternate Li^6 Reflux Systems

1) The Li(Hg) can be contacted with anhydrous HCl gas and EDA to produce the following:

$$Li(Hg) + HCL + EDA \longrightarrow Hg + LiCl_{EDA} + H_2$$

This system is not too good because:

a) Difficulties of preparing and handling anhydrous HCl gas.

b) Difficulties involved in operating a continuous gas - metal - organic contactor

c) During the progress of the above reaction alkyl ammonium amalgam is formed.

The system has the advantage of not requiring the addition of NaCl and subsequent decomposition of NaHg to produce undesirable quantities of H_2 and NaOH. No decision was made concerning work on this alternate.

2) Another system suggested:

$$Li(Hg) + Hg^{+} + Cl^{-} + EDA \longrightarrow Hg + Hg + LiCl_{EDA}$$

however scouting work has indicated that $HgCl_2$ is quite insoluble in EDA.

e. Materials of Construction

Materials of construction have not been studied, but in all probability the Li^6 reflux system should be built of stainless steel for the pilot plant. The NaCl columns should probably be Type 316; Mathieson should be checked to determine materials for the NaHg decompose. See note in Section 3.15 concerning stainless steel corrosion for this system.

3.15 General Problems in the CR System

1. Surge capacity for both streams must be provided in the cascade. Shacter suggests that major surge capacity be installed near the feed point or even after the stripping section. It will also be necessary, however, to install hold tanks at taper points in the cascade or possibly more frequently so that the system can be shut down without a subsequent major loss in enrichment. Each surge tank must be provided with means for bleeding its contents back into the cascade, preferably at an automatically controlled rate.

2. Obviously, pumps and other prime movers must be developed.

3. Problems of process control have not been studied. In fact, in most cases, there are no obvious variables that can be used as the design variable to establish automatic control. Manual control of the pilot plant may be possible, but at present it seems most difficult if large numbers of skilled operating personnel are not available. Garretson has pointed out that the corrosion resistance of stainless steel is very poor in oxygen free chloride solutions. Corrosion products from stainless steel may lead to serious hydrogen overvoltage problems in the amalgamaker.

4. It is imperative that long term static and dynamic corrosion studies be started for most process systems in order to develop the most economical materials of construction for a full scale plant. Actual corrosion of the test materials is not all that must be learned from these studies; for materials selected, the effects of corrosion products introduced into the cascade must be evaluated.

5. Lab studies on process impurities introduced by various reagents must be made.

6. Sampling techniques must be studied and developed.

7. Analytical methods must be developed and evaluated statistically. Analytical facilities must be provided capable of handling sample loads from two pilot plants.

8. Methods of disposal for such wastes as H_2, O_2, Cl_2, and NaOH must be provided.

9. All electrical equipment should be explosion proof.

10. Safety procedures and design requirements must be developed.

11. If possible, alternates to dry helium and dry hydrogen should be developed. Nitrogen or dry air offer much cheaper or safer systems. Ammonia gas atmospheres should also be studied.

12. Statistical data must be collected; therefore, the pilot plant operation requires statistical analysis to define data collection techniques, accuracy and precision.

13. Ventilation air in large quantities may be required.

14. Special non-sparking tools and non-static collecting shoes should be provided.

15. The entire instrument control system requires statistical analysis to define accuracies and precisions for a given plant length and width.

3.2 The Dual Temperature Process - Summary of Pilot Plant Discussion

3.21 Proposed Pilot Plant Size

Capacity: 400 gms Li per day at 26% enrichment

Enrichment: amalgam phase, 26% Li^6

Stripping: amalgam phase, 95% Li^7

Probable column sizes: Stripping: 6" - 6"
Enriching: 8" - 8"
6" - 6"
5" - 5"
4" - 4"
$2\frac{1}{2}$" - $2\frac{1}{2}$"

Feed: amalgam phase prepared from naturally occuring lithium containing 92.8% Li^7 and 7.2% Li^6

Preliminary calculations: not now available

Schematic pilot plant flowsheets:

Figure 2. "S" Process
Figure 3. "GS" Process

3.22 Objectives of Pilot Plant

1. Determine the operability of dual temp process as shown for the "S" and "GS" processes and decide which is optimum based on economy and efficiency.

2. Collect capital and operating cost information.

3. Prove instrumentation, pumps, controls.

4. Develop necessary equipment prototypes .

5. Provide data adequate for scale up to plant size.

3.23 Basic Data for DT System

This process, like the chemical reflux process, is based on the countercurrent contacting in a series of pulse columns of a lithium amalgam with a LiCl solution in ethylene diamine. Under such conditions, the Li^6 isotope tends to concentrate in the amalgam phase while the Li^7 isotope tends to concentrate in the amine phase. The separation factor is about 1.05 at 26°C, and 1.028 at 99°C. In the chemical reflux process the problem of refluxing the streams is handled by chemically recombining the streams leaving the pulse column and returning them to the column. In the dual temperature process, however, advantage is taken of the variation of the separation factor with temperature; a stream of amalgam is passed countercurrently to an amine stream at a low temperature and, in a parallel column, again at a high temperature. The higher separation factor at the lower temperature makes possible the concentration of Li^6 in the amalgam phase at this temperature and, contrariwise, its return to the amine phase at the higher temperature. Thus, an alternate enriching process and stripping process can be carried out on the amalgam phase in two series of columns. This process is basically simpler than the chemical reflux process described above, since the involved chemistry that is inherent in the chemical reflux process is unnecessary in the dual temperature process. The dual temperature process, however, suffers under the disadvantage of having a considerable lower overall separation factor, approximately 1.01, than does the chemical reflux process. This lower separation factor necessitates the use of many more extraction stages to effect the desired separation than are needed for the chemical reflux process. The width of the plant must also increase since the $\left(\frac{V}{D}\right)$ varies with $(\alpha - 1)$.

1. Properties of EDA, $LiHg_2$, Hg, LiCl, LiOH are given in Section 3.13 for CR process.

2. Temperature of operation and separation factors of hot-cold column pairs for pilot plant design purposes:

	Cold Column	Hot Columns
Temperature	26°C	99°C to 110°C
α, use	1.048 ± 0.002	1.028 ± 0.010

Overall $\alpha = 1/2\left(\frac{\alpha_c}{\alpha_h} - 1\right) + 1$

or a close approximation:

$$= 1 + \frac{\alpha_c - \alpha_h}{2}$$

= 1.01 use

[redacted]

3. Lithium amalgam concentration (design):

0.5 M Li in Hg (gm. mols/liter)
possibly 0.75 M.

4. LiCl Concentration in EDA (design): 0.25 M as determined by cold column operation

3.24 Detailed Description and Data for Major Process Units

The following sections summarize decisions on each major process unit. It has been assumed that both "S" and "GS" piping systems will be installed as shown in Figures 2 and 3.

1. The Pulse Column Pairs

The pulse columns used in the dual temperature process are to be arranged in two interconnected series, one series being kept at a temperature of about 26°C and the other series at a temperature of about 110°C. Two different methods of distributing the flow of the amalgam and amine phases through the pulse columns are to be investigated - the "S" process and the "G-S" process, which are shown schematically in Figures 1 and 2. It can be seen that the flow pattern of the amalgam phase is the same in both processes, that the difference in the two processes is the flow pattern of the amine phase.

a. The "S" Process

In the "S" process the pulse columns are arranged in pairs of hot and cold columns of equal sizes. The amine solution flows in a cyclical pattern between the pairs of columns; that is, the flow is from a hot column, through a heat exchanger, through the corresponding cold column, back through the heat exchanger, and back into the hot column to complete the cycle. The flow of the amalgam phase is from one cold column to the next on through the series of cold columns, through a heat exchanger, through each of the hot columns in series, through another heat exchanger, and back into the cold columns. In addition, there is a flow of amalgam from each of the cold columns to its paired hot column. The net result is that less amalgam (and less amine) is flowing through the columns at one end of the system than at the other; consequently, these columns can be made smaller. The flows of the different streams and the arrangement of the columns can best be seen by referring to Figure 2.

The "S" process requires a greater energy expenditure than the "GS" process since the amine streams in each column set must be both heated and cooled in passing between the hot and cold columns. However, the "S" process reduces the possibility of circular flow in the cascade, i.e. the greater number of cross-over points reduce the possibility

of having gradient differentials in lithium horizontally through the cascade as well as vertically. Such horizontal gradients cause an "eddy" in the cascade which wastes separation potential of the stages of the cascade which are included in the eddy loop.

b. The "GS Process

The "GS" process was proposed to minimize frequent heat transfer and expenditures of energy in the dual temp cascade. In this process the flow of amalgam is exactly the same as for the "S" process. The amine flow, however, instead of being just between a pair of hot and cold towers is a mirror image of the amalgam flow. That is, the amine flows countercurrently to the amalgam through each of the hot towers in series, through a heat exchanger, through each of the cold towers, through another heat exchanger, and back into the hot columns. Also, as is the case with the amalgam, there is a side flow of amine from each hot tower to its corresponding cold tower. The arrangement of this process is shown in Figure 3.

Control of the "GS" process must be much more exacting than in the "S" process since the possibility of circular flow in the cascade is greatly increased by having four streams (2 sets of 2 streams each) that are not mixed at frequent "horizontal" points in the cascade. It is more possible to obtain a difference between concentration of the set streams which enter and comprise one effective stream in a combined hot-cold stage in the "GS" system than in the "S" system.

Because of the piping arrangements necessary for the "GS" system, transfer of heat for maximum efficiency is difficult particularly because of the markedly lower heat capacity of Hg as compared with EDA. In all probability it will be difficult to provide practically the theoretical efficient of heat utilization inherent in the "GS" system.

The pilot plant columns will be built so that it is possible to test both the "S" and "GS" systems. Several feed points for amalgam in both the hot and cold columns will be installed in order to measure α by difference in either column.

c. Column Data

Column data are the same as given for the CR reflux process in Section 3.14 (1).

2. Lithium hydroxide electrolyzer - amalgamaker for feed

This unit is described in Section 3.14 (2). One unit can be used to prepare feed for both the CR and the DT processes.

It has been assumed that feed will be introduced to the top of the feed cold tower as amalgam. It is possible that feed could be introduced in the amine phase.

3. Product decomposer - production of Li^6 OH rich solution

Similar to unit described in Section 3.14 (3). A separate product decomposer will be required for the DT process.

For design purposes it will be assumed that product is drawn off as the amalgam from the bottom of the cold tower on the Li^6 end of the plant. It is possible that feed could be taken off in the amine phase.

4. Stripper bottoms decomposer - Li^7 OH rich solution

The bottoms decomposer is similar in function and design to the product decomposer, but will be of larger capacity.

It has been assumed that Li^7 Hg will be withdrawn from bottom of the last hot column in the cascade. It is possible that waste could be withdrawn in the amine phase.

5. EDA - LiCl Make up System

EDA must be dried and prepared for use as described for the CR system. In fact, a common make-up system for charging both pilot plants can be used. LiCl must be dried and dissolved in EDA as described for the CR process.

6. EDA Purification

No data exist for theuseful life of EDA in the dual temp system. In the CR process EDA is distilled as part of the reflux system, but in the CR process EDA need never leave the cascade. It is possible that a small portion of the EDA should be purified by techniques not now defined to prevent possible impurity buildup in the cascade.

7. Materials of Construction

Stainless steel will be used throughout in the pilot plant except for possible corrosion test sections.

3.25 General Notes and Problems in DT Process

It is intended that the problems connected with the dual temperature process will be investigated in both a one cm. column and a one inch column at Y-12 and in a pilot plant that is to be built. The following information is to be obtained at one or more of these installations.

1. A satisfactory plate size, hole size, and plate spacing are to be determined. Optimum sizes and spacing are to be determined if time allows.

2. Flooding rates are to be determined for different types of packing. A plot of flooding rate for various temperatures is to be made for the one inch column only; scale up factors will be used to make this information available for plant design.

3. Separation factors will be measured at different temperatures.

4. The dual temperature process is sensitive to variations in flow, the "G-S" method in particular being quite sensitive. It is believed that it will be necessary to control the flow within 1%; therefore, means of accurately measuring and controlling the flow of amine and amalgam will be studied. In addition, the effect of larger variations in flow will be investigated.

5. Equilibrium times will be determined.

6. HTU's or HETS' will be determined.

7. It is unknown whether or not it is necessary to build the paired cold and hot columns the same length. It is quite possible that the cold column can be smaller than the hot column and still perform the same function; it is equally possible that the hot column could be made smaller. For this reason, it is proposed that in the construction of the pilot plant a provision be made in one pair of hot and cold columns for the amalgam to be fed to each column at any one of several levels. In this way the effective heights of these columns can be varied and the correct size relationship determined.

8. The dual temperature processes will be investigated with special emphasis being placed on problems connected with the start-up of the process, the repair of units while on stream, the storage of material during shutdown, and surge capacity. The possibility of by-passing a tower when repairs are needed instead of shutting down the plant will also be investigated.

9. The experience of the Y-12 group has been that EDA tends to form decomposition products when heated to temperatures of 110°C or above. This decomposition will be investigated more fully; means of retarding it will be studied, and, if necessary, a method of purifying the EDA will be developed. There is an obvious advantage in running the hot column at higher termperature to increase the effective α.

10. Exploratory work will be done on the possibility of using the amine phase as the feed stream to the process rather than the amalgam phase as now proposed. In addition, thought will be given to the possibility of altering the "S" process so that the amine phase moves up the series of towers rather than the amalgam phase.

11. A corrosion study program must be initiated to determine corrosion rates in amine-amalgam mixtures. These studies will be made under dynamic, not static, conditions and will be continued for from 6 to 9 months. In addition, it is proposed that some section of the pilot plant be made of mild steel or the materials less expensive than stainless steel as a further test of corrosion problems.

In addition to the above, the following general problems listed in Section 3.15 also apply to the DT process: 1,2,3,5,6,7,8,9,10,11, 12,13,14,15.

4.0 Proposed Location of the Pilot Plants

The Orex pilot plant will be located at X-10 in Building 4501, in space where future radioisotope development cells will eventually be installed.

The main room is approximately 36' x 35' x 60' high (to roof chord). In addition to this, there is space surrounding this large room and opening onto it with 14' headroom and 4698 ft^2 in area. To the east of the main room a platform raised 2'6" off of finished floor grade provides additional space having headroom of 11'6" and area of 2360 ft^2.

This space is separated by concrete block and brick walls from other operating parts of the building. Services such as steam, water, air, electricity are run in. Waste tunnels leading to the exterior of the building are located on the east and south sides of the space. An areaway from grade is located on the west side of the building.

Ventilation will have to be installed in this area. A craneway is provided; the top of the craneway rail is 57'2-1/2" from floor level. The crane hook at maximum lift clears the floor by 52'6".

Four walls are free and uncluttered for the entire height of the high bay. Support platforms and structural steel framing for balconies, walkways, etc., must be installed.

Figure 5. is a rough outline sketch of space available.

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H. O. Weeren

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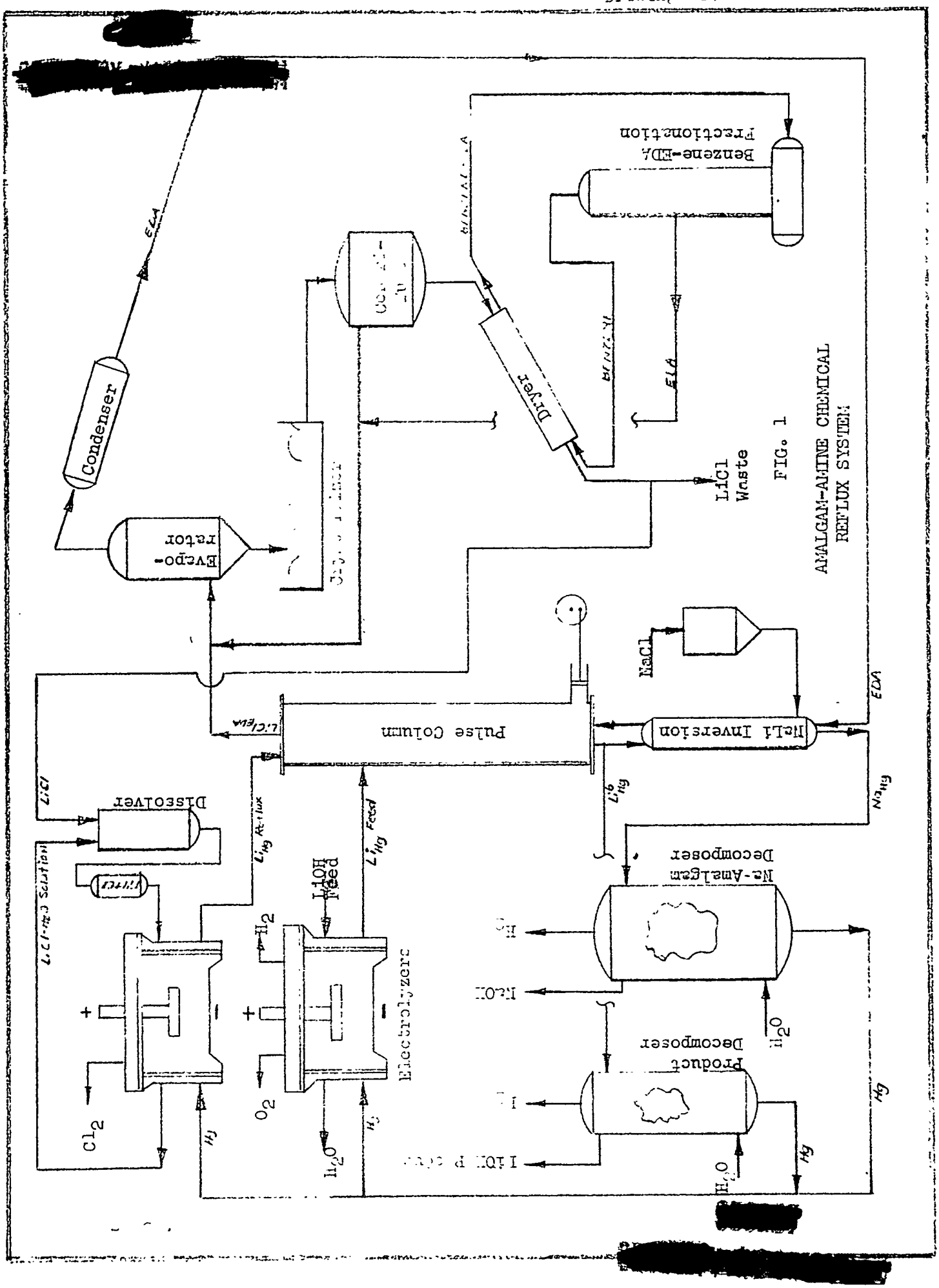
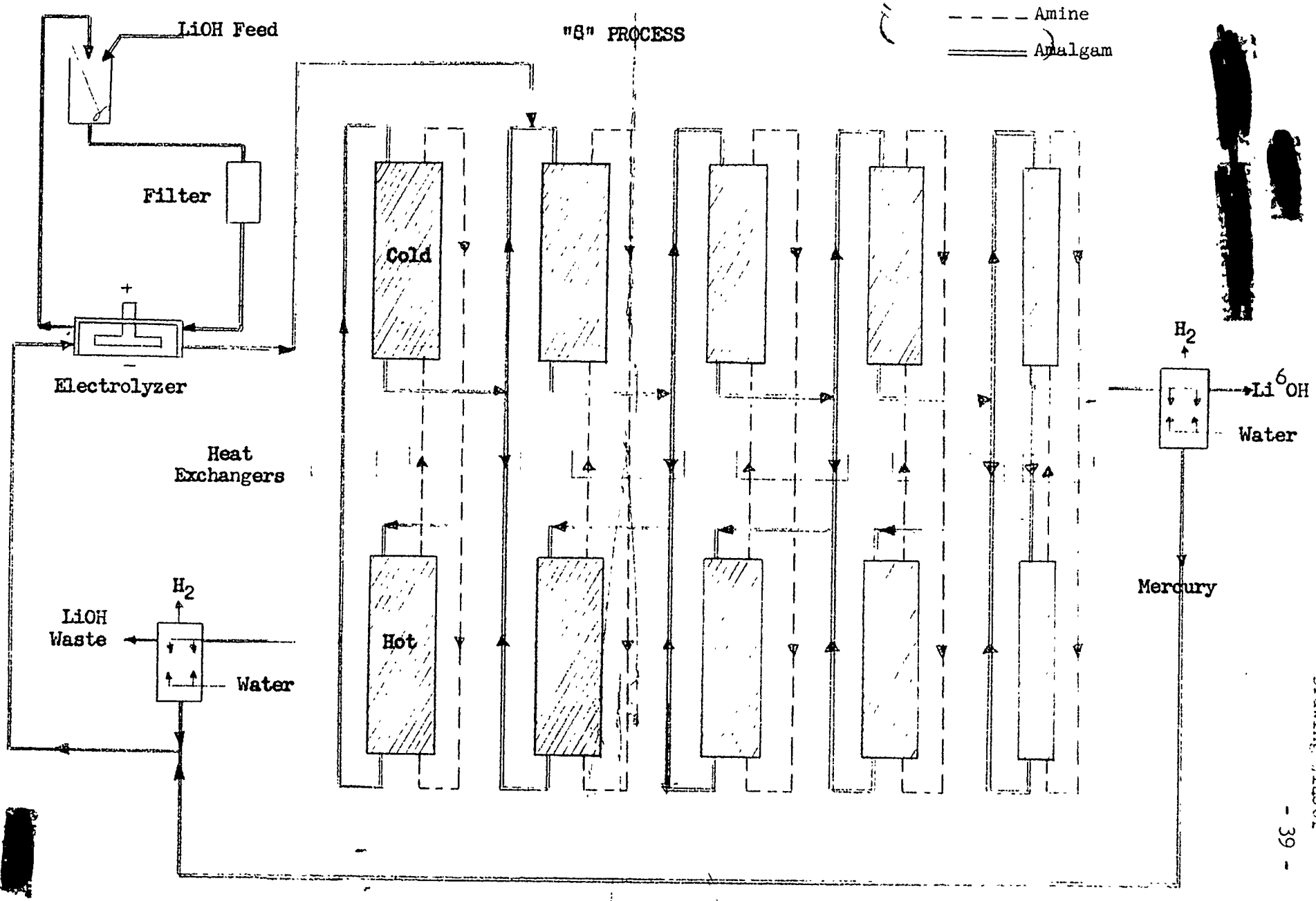


FIG. 1

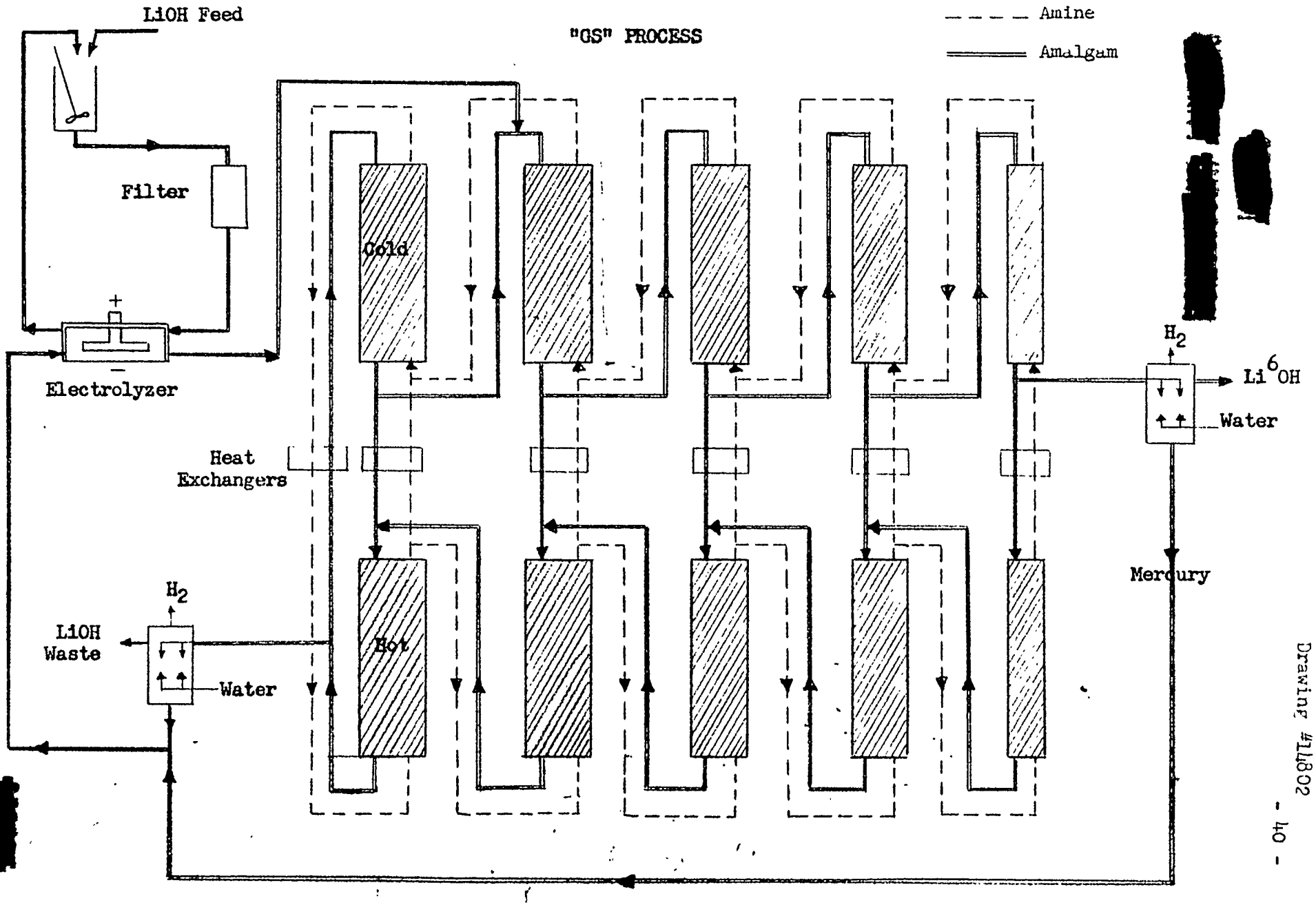
AMALGAM-AMINE CHEMICAL REFLUX SYSTEM



AMALGAM-AMINE DUAL TEMPERATURE SYSTEM

FIGURE 2

Drawing #L1301



AMALGAM-AMINE DUAL TEMPERATURE SYSTEM

FIGURE 3

Drawing #11802

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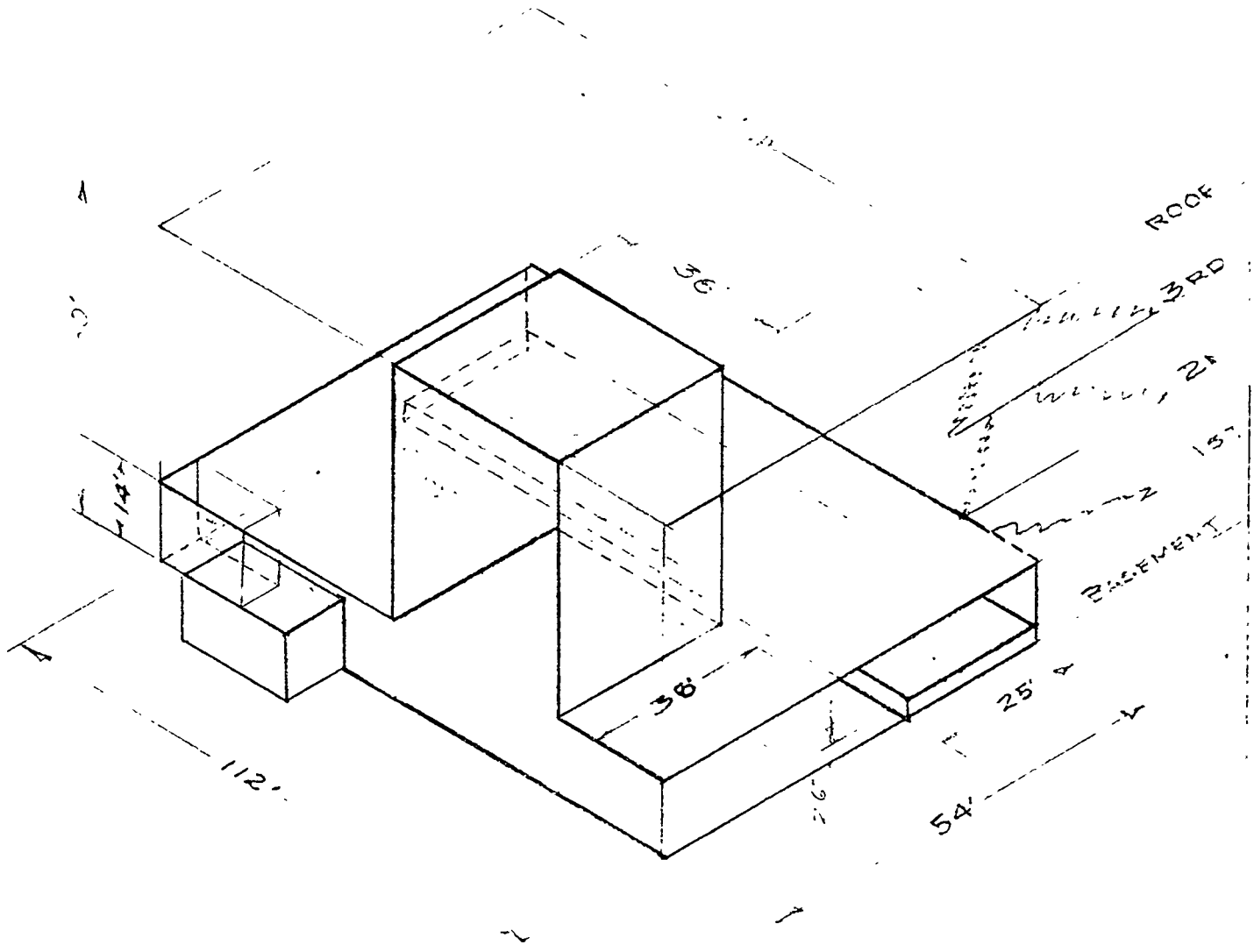
FIGURE 5.

SPACE FOR PILOT PLANT

BLDG. 4501



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APPENDIX I

Proximate Comparison of Elex, Relex A, Relex B, Dual Temperature Processes

Relex A. - Assume HTU (HETP) = to ~6 ft.
Relex B. - Assume HTU (HETP) = to ~1 ft.
Capacity - Same as Elex process now being designed.

1. General Considerations

Item	Elex	Relex A	Relex B	Dual Temp
Agitators	90,000	219	43	0
Baffles	90,000	219	43	0
Blenders	yes	no	no	no
Heat exchangers	no	no	no	yes
Piping	large	small	small	large
Pumps	114	94	~20	243
Circular Flow	yes	no	no	yes
Control	precise< 2%	normal	normal	precise< 2%
Total lined wall in contact with sol at feed point	120'	6'	6'	5.25'
$\gamma(\alpha-1)$	0.05	0.05	0.05	0.013
N (relative)	1	1	1	7.7
V (relative)	1	1	1	1.93

APPENDIX I (Continued)

2. Cost Estimates

Construction	$31-35 X 10^6	$12.5 X 10^6	$4.3 X 10^6	$10.43 X 10^6
Equilibrium time($)	$1.3 X 10^6	.9 X 10^6	.9 X 10^6	.4 X 10^6
Operating costs/yr (excluding amortization)	4.6 X 10^6	1.86 X 10^6	1.1 X 10^6	1.5 X 10^6
Operating Cost including 5 yr. amortization	$11.2 X 10^6	4.4 X 10^6	1.95 X 10^6	3.6 X 10^6

Note: All data taken from notes from talk by J. Shacter, March 27, 1952

APPENDIX II

Calculations for a Chemical Reflux Pilot Plant

by G. H. Clewett

Basis of Design = 50 gal./hr EDA

Evaporation System

50 gal./hr = 190 liters/hr.

(190) (7) (.25) = 330 g Li/hr or (330) (6) = 1980g LiCl/hr or

[(2.2)(1.98) $= \sim$ 4.4 lbs/hr]

$$\left(\frac{V}{D}\right)_{min} = \frac{(.95 - .072)\ [1 + (.05)(.072)]}{(.05)\ (.072)\ (.928)}$$

$$= 262$$

$$\left(\frac{4}{3}\right)(262) = 350 = \left(\frac{V}{D}\right)_{actual}$$

$$D = \frac{330}{350} = .94\text{g/hr} = 22.5\text{g/day} = \sim .05 \text{ lbs/day}$$

Electrolysis System

$$\frac{330}{7} = 47.1 \text{ mols/hr} \quad \frac{(47.1)\ (96{,}500)}{3600} = 1260 \text{ amps minimum}$$

at 90% efficiency $\sim$ 1400 amps required.

at .5 molar

$$\frac{330}{3.5} = 94 \text{ liters/hr of .5 molar amalgam } (\sim 25 \text{ gal/hr})$$

Columns

at 1400 gal./ft^2/hr amalgam flow

$$\frac{(25)\ (144)}{1400} = 2.57 \text{ in.}^2 \text{ required at widest part of plant}$$

[redacted]

[redacted]

APPENDIX II (Continued)

$$\frac{\pi D^2}{4} = 2.57$$

$$D^2 = \frac{(4)\ (2.57)}{3.14} = 3.28$$

$$D = 1.81"$$

Allowing .2" for central support rod

$$D = 1.81 + .2 = 2.01"$$

$$\frac{V}{D} = 350$$

$$\frac{D}{V} = .00285$$

Square off at .5 conc. (.072 to .50)

$$x_o = \frac{\left[(\gamma - 1) + \frac{D}{V}\right] - \sqrt{\left[(\gamma - 1) + \frac{D}{V}\right]^2 - (4)\ (\gamma - 1)\ \frac{D}{V}}}{2(\gamma - 1)}$$

$$= \frac{.05 + .00285 - \sqrt{(.05 + .00285)^2 - (4)\ (.05)\ (.00285)\ (.95)}}{(2)\ (.05)}$$

$$= \frac{.05285 - \sqrt{.00279312 - .00054150}}{.1}$$

$$= \frac{.05285 - .04746}{.1} = \frac{.00539}{.1} = .0539$$

$$x_1 = \frac{.05285 + .04746}{.1} = \frac{.10031}{.1} = 1.0031$$

$$N = \frac{1 - .00285}{(.05)\ (1.0031 - .0539)} \ln \frac{(.5 - .0539)\ (1.0031 - .072)}{(1.0031 - .5)\ (.072 - .0539)}$$

$$= \frac{.99715}{(.05)(.9492)} \ln \frac{(.4461)\ (.931)}{(.5031)\ (.0181)}$$

$$= (21.01)\ (2.303)\ (\log 45.7)$$

$$= (21.01)\ (2.303)\ (1.6599)$$

$$= 80.5 \text{ actual stages needed going from .072 to .5}$$

[redacted]

APPENDIX II (Continued)

Top squared of section (.50 to .95)

$$\left(\frac{V}{D}\right)_{min} = \frac{(.95 - .5)\left[1 + (.05)(.5)\right]}{(.05)(.5)(.5)}$$

$$= \frac{.46125}{.0125} = 37$$

$$\left(\frac{V}{D}\right)_{act.} = 1.6\left(\frac{V}{D}\right)_{min} = (1.6)(37) = \sim 60$$

$$D = \frac{190}{350} = .542 \text{ l./hr}$$

$$V = (60)(.542) = 32.5 \text{ l./hr} = 8.6 \text{ gal./hr}$$

$$\frac{8.6}{1400} \times 144 = .88 \text{ in.}^2$$

$$D = \frac{\sqrt{(4)(.88)}}{\pi} = \sqrt{1.12} = 1.06\text{" or 1-1/4" pipe to}$$

$$\frac{V}{D} = 60 \quad \frac{D}{V} = .0167$$

$$x_o = \frac{(.05 \quad .0167) - \sqrt{(.05 + .0167)^2 - (4)(.05)(.0167)(.95)}}{.1}$$

$$= \frac{.0667 - \sqrt{.004449 - .003173}}{.1}$$

$$= \frac{.0667 - .0357}{.1}$$

$$= \frac{.0310}{.1} = .31$$

$$\frac{x_o}{x_1} = \frac{.1024}{.1} = 1.024$$

$$N = \frac{1 - .0167}{(.05)(1.024 - .31)} \ln \frac{(.95 - .31)(1.024 - .5)}{(1.024 - .95)(.5 - .31)}$$

$$= \frac{.9833}{(.05)(.714)} \ln \frac{(.64)(.524)}{(.074)(.19)}$$

$$= (27.6)(2.3)(\log 23.8)$$

$$= (27.6)(2.3)(1.377)$$

$$= 87.3 \text{ actual number of stages needed from .50 to .95}$$

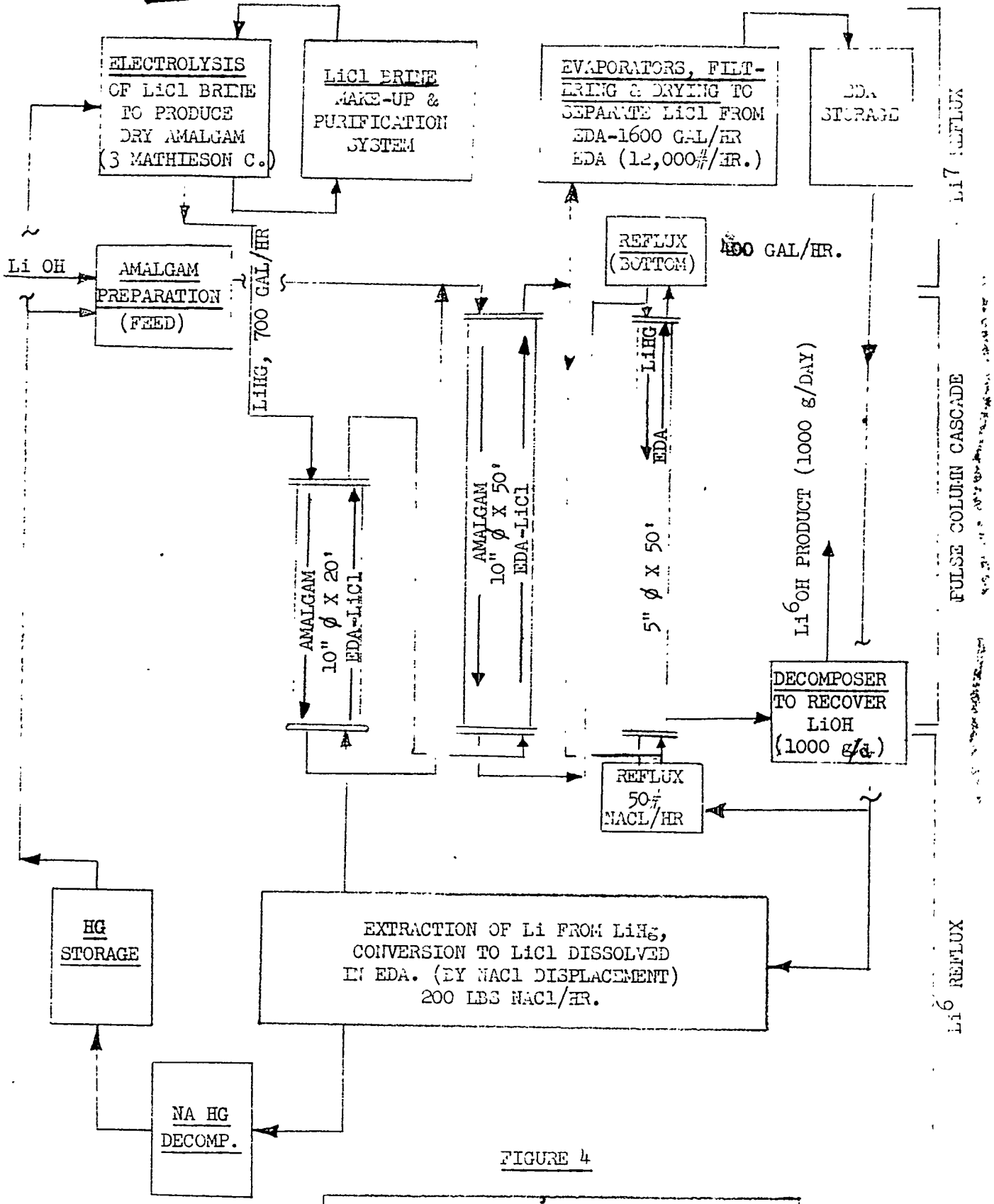

FIGURE 4

AMALGAM-AMINE REFLUX SYSTEM PLANT SCALE

FROM: MATERIALS CHEM. DIVISION

DATE: 4-16-52

X-426 (Revised 1-52)

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DATE: May 23, 1952

SUBJECT: OREX: Slurry Pulse Column for Amalgam Inversion--
Quarterly Report for Period 4/1/52 to 5/10/52

TO: F. L. Steahly

FROM: R. W. Horton, A. C. Jealous

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TO: F. L. Steahly -2- Chemical Technology Division
Unit Operations Section

FROM: R. W. Horton, A. C. Jealous

Report Period: 4/1/52 to 5/10/52
(Work not started until 4/1/52)

QUARTERLY REPORT

CT-75

Title: OREX: Slurry Pulse Column for Amalgam Inversion

Work By: R. W. Horton, A. C. Jealous

Secret Notebook No.: 2137-G

1.0 Introduction

In the chemical exchange process for the separation of lithium isotopes, a lithium-mercury amalgam is contacted by a solution of a lithium salt in an organic solvent. Ethylene diamine is the most suitable solvent of those which have been investigated. In the process an isotopic exchange reaction takes place with Li^6 favoring the amalgam phase slightly more than Li^7 does. A high reflux of Li^7 at one end of the column and of Li^6 at the other is required. Pulse columns are proposed for the exchange operation. The present study is concerned with the Li^6 reflux and in particular with the displacement of Li^6 from the amalgam phase with Na from a slurry of NaCl in EDA by countercurrent contacting in a pulse column, thus recycling the Li^6 back to the exchange column in the EDA phase.

The use of a NaCl slurry rather than a solution is necessary because of the low solubility of NaCl in EDA (0.05M @25° C. and 0.02°M @100° C.).

2.0 Summary

Better than 95% Li inversion was obtained in a brief pulse column test made to scout the use of a slurry of NaCl in EDA to displace the Li from Li (Hg). Li^6 inversion by Na exchange is required to form the Li^6Cl-EDA solution necessary for effecting Li^6 reflux and enrichment in the chemical Reflux process for isotopic separation and recovery of Li^6 from LiCl feed. The scouting run was only 12 minutes duration, and was carried out at 100° C.

A 0.5 in. stainless steel pulse column with variable contactor height is being erected at Y-12 for further, more detailed study of the inversion operation. This installation will permit runs of up to 2 hours duration and will be complete by June 1, 1952.

3.0 NaCl-EDA Slurry Column Behavior

Preliminary investigations in a glass column showed that a salt slurry containing particles as large as 40-60 mesh could be handled through a Milton-Roy pump and could be made to travel up a column countercurrent to an amalgam flow. It was also learned that salt particles as small as 150-200 mesh could be settled out in an enlarged chamber at the top of the column.

4.0 Slurry Inversion Column Test

A trial run was made on May 7, 1952 in a column at Y-12 temporarily available from the DT process study. This column is 24 feet high, 0.87" I.D. (0.0042 sq. ft. cross section), has 20 mesh screen plates spaced 1" apart, and is jacketed for steam heating. Milton-Roy pumps were used for both feed streams and for pulse generation.

A 4 in. dia. glass pipe dissolver tank equipped with a vertical agitator was used to prepare the slurry, which was made up with 978 grams of minus 150 mesh NaCl in 11 liters of EDA, giving a 1.5 molarity. After a twenty-minute dissolving period, the slurry was pumped through the column in upflow and returned to the dissolver tank so that slurry was constantly recycling during the run.

The amount of amalgam available was three liters of 0.65 Li molarity. Amalgam was pumped from a head tank through the column to a separate receiver so that a single-pass result could be obtained.

Conditions of the first run were as follows:

Temperature	100° C.
Slurry flow rate	600 cc/min. (2300 GSFH)
Amalgam flow rate	250 cc/min. (960 GSFH)
Pulse rate	200 c.p.m.
Pulse Amplitude	1"

Samples of amalgam effluent were taken every three minutes until a single pass had been completed. Results are as follows:

	Li/Na Molarity
3 minutes	0.026
6 minutes	0.025
9 minutes	0.023
12 minutes	0.22

At the end of this run the column and the slurry were cooled to 32° C. and the run was repeated using the same amalgam. The pulse rate was reduced to 128 c.p.m. for the cold run. Samples were taken after a single pass and the amalgam was then recycled for three more passes. Thus, the first four results below represent time intervals during the second pass (counting the hot run as the first) and the fifth and sixth samples represent the end of four and five passes, respectively:

4.0 Slurry Inversion Column Test (Continued)

	Li/Na Molarity
#1	0.022
#2	0.023
#3	0.022
#4	0.021
#5	0.022
#6	0.021

Apparently no significant additional inversion was accomplished after the first run. There is some question regarding analytical procedures for low concentrations of lithium in amalgams containing sodium, which may have a bearing on these results. The Y-12 analytical development is investigating this problem.

R. W. Horton /mh
R. W. Horton

A. C. Jealous /mh
A. C. Jealous

RWH:mh

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DESIGN AND ECONOMIC STUDIES - PROCESS DESIGN SECTION
MAY 10, 1952 - AUGUST 10, 1952

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SUBJECT: OREX PROJECT QUARTERLY REPORT
DESIGN AND ECONOMIC STUDIES
PROCESS DESIGN SECTION
MAY 10, 1952 - AUGUST 10, 1952

0.0 ABSTRACT

Preliminary design calculations for the dual temperature full scale plant have been completed for the purpose of an initial cost evaluation of the process. These calculations indicate that the dual temperature plant would require an initial investment of $35,535,900.00, and that the annual operating costs would be on the order of $12,646,000.00.

Preliminary design calculations of the chemical reflux full scale plant have not been completed to the point where a cost evaluation can be made.

1.0 INTRODUCTION

The Orex process for the separation of the isotopes Li^6 and Li^7 can be classified into two different systems, the dual temperature system, and the chemical reflux system, according to the mode of operation. These two processes are in competition with each other for performing the same separation, and due to the urgency of the Orex program, it is necessary that a quick estimate of the cost of each process be made available. The results of this cost estimate would then be available for aiding in a decision concerning the program on which emphasis should be placed.

In order to establish a comparable basis for the estimation of the two processes, it was established that both designs should be made at full scale plant production, at the same product enrichment, and using the same stage height. Calculations have been made to determine the sizes of the various pieces of process and auxiliary equipment. Whenever sufficient information was available, specific equipment has been specified. The preliminary design calculations for the dual temperature full scale plant were used in a cost evaluation to determine initial investment and yearly operating costs. At the time of this writing, the chemical reflux full scale plant calculations have not progressed to the point where a cost estimation can be made.

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SUBJECT: PHYSICAL PROPERTIES OF MATERIALS FOR OREX PROCESS

The accompanying tabulations and graphs present useful data on the several chemicals employed in the Orex process. These data include such properties as solubilities, heat capacities, viscosities, thermal conductivities and other pertinent engineering data and physical constants.

The compilation of these data was undertaken because of the need for a single composite source of engineering information. This document, therefore, is the result of a review of Orex documents and reports, of literature searches, and of personal communications with members of the Materials Chemistry Division and the Chemical Technology Division. The writers wish to acknowledge the numerous contributions to these data by X-10 and Y-12 personnel through their efforts in experimentation and library research.

Herman O. Weeren

H. O. Weeren
Process Design Section
Chemical Technology Division

William L. Carter

W. L. Carter
Process Design Section
Chemical Technology Division

WLC:amh

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TO: F. L. Steahly and F. L. Culler DATE: March 23, 1953

FROM: W. L. Carter

SUBJECT: MERCURY REQUIREMENTS FOR OREX OPERATIONS

Mercury requirements for the Orex Test Facility, twenty-four inch diameter dual temperature columns and Unit Operations experimental program have been determined and are detailed in the attached tabulation. However, the requirements may be summarized as follows:

	Mercury Requirement	
	Gallons	Pounds
Orex Test Facility Operating Inventory	435	49,200
24-Inch Diameter Columns Operating Inventory	634.6	71,585
Reserve for Test Facility and 24-Inch Columns	650	73,500
Unit Operations Experimental Program	400	45,200
Total	2119.6	239,400
*Estimated Test Facility Loss per Month	50	5,650
Current Inventory	500	56,500

*This loss will occur only in magnesium reflux operation, and it is quite likely that the losses will not be this great.

It should be pointed out that the operating inventory for the Orex Test Facility and 24-inch diameter columns should be on hand by July 1, 1953. This amounts to 1069.6 gallons or 120,785 pounds. A current inventory of 500 gallons (56,500 pounds) is available in the X-10 area, and it is believed that this quantity is sufficient to take care of Unit Operations' requirements. Since the Unit Operations' program will not consume mercury, this inventory will be available for Orex Test Facility use after the Unit Operations' program is completed.

[redacted]

[redacted]

It should be noted that 650 gallons (73,500 pounds) of clean mercury storage is being provided. This quantity is sufficient to replace the entire operating inventory of either the Orex Test Facility or the 24-inch diameter columns.

Previous mercury requirements for the Orex program at X-10 have been reported in ORNL Central Files document 52-10-208. The information in document No. 52-10-208 is superseded by estimates quoted in this memorandum.

William L. Carter

W. L. Carter
Process Design Section
Chemical Technology Division

WLC:amh

[redacted]

[redacted]

MERCURY INVENTORY TEST FACILITY

Vessel	Hg Inventory Gallons	Hg Inventory Pounds
Product Mixer Settlers	50.5	5,706
Product Amalgam Tanks	30	3,400
Product Decomposer	10	1,130
Product Amalgam Recycle Tanks	30	3,400
NaHg Decomposer	26	2,940
Clean Hg Storage	650	73,500
Hg Cleanup Tower	11	1,330
Hg Drying Column	1	113
Hg Accumulator in NaOH Desolvation System	3.2	360
Lines and Pumps (5% of above)	40.6	4,587
Sub Total	852.3	96,466
Pulse Columns	21.6	2,440
Surge Tanks	6.8	765
Lines and Pumps (5% of above)	1.4	158
Sub Total	29.8	3,363
Waste Reflux Mixer Settlers	122	13,800
Mg Dissolvers	39.2	4,430
Amalgam Surge Tank	25	2,830
Decomposer	5	565
Filter	2	226
Lines and Pumps (5% of above)	9.7	1,096
Sub Total	202.9	22,947
TOTAL	1,085	122,776

[redacted]

[redacted]

MERCURY INVENTORY 24-INCH COLUMN SET

Vessel	Hg Inventory Gallons	Pounds
24-inch Pulse Column (cold) (DTC-100)	96.5	10,900
24-inch Pulse Column (hot) (DTC-101)	77	8,700
Mercury-Amine Heat Exchanger (DTC-201)	117	13,100
Mercury-Amine Heat Exchanger (DTC-200)	90	10,150
Mercury Heater (DTC-204)	10.6	1,220
Mercury Cooler (DTC-205)	18.3	2,070
Surge Tank (DTC-503)	20	2,260
Surge Tank (DTC-500)	20	2,260
Recycle Tanks (DTC-504, 505, 506)	100	11,300
Amalgam Storage Tanks (CR-533, 549)	55	6,215
Sub Total	604.4	68,175
Inventory in lines and pumps (5% of above)	30.2	3,412
TOTAL	634.6	71,587 ✓

MERCURY INVENTORY UNIT OPERATIONS

Total Inventory	400 gal	45,200 lbs ✓
Estimated Loss (total)	1 gal	113 lbs

OREX TEST FACILITY USAGE

Estimated usage	50 gal/mo	5,650 lb/mo

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TO: F. L. Steahly

DATE: October 30, 1952

FROM: H. O. Weeren

SUBJECT: REVISED MERCURY REQUIREMENTS FOR OREX PROGRAM - CHEMICAL TECHNOLOGY DIVISION

4501

The mercury requirements for the Orex program, both the test facility and the 24 inch column set, have recently been reviewed and have been found to differ considerably from the original estimates. These original estimates and a summary of the latest estimate are tabulated below; the details of the most recent survey are given on the following pages.

	ORIGINAL ESTIMATE	NEW ESTIMATE
24 inch column set	90,500 lb	111,250 lb
4501 Test Facility (pilot plant)	28,200 lb	91,250 lb
TOTAL	118,700 lb	202,500 lb

Delivery dates for the required mercury should be as follows:

February 15, 1953	40,000 lbs for the column section of the test facility
April 15, 1953	162,500 lbs for the rest of the test facility and for the 24 inch column set.

H. O. Weeren

H. O. Weeren
Process Design Section
Chemical Technology Division

HOW:amh

cc: F. L. Culler
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MERCURY INVENTORY

24 inch columns

Hot Column - 50 ft high, 402.1 sq. in. area, 11% amalgam holdup

$$\left(\frac{402.1}{144}\right)(50)(.11) = 15.36 \text{ cu ft}$$

Cold Column - 50 ft high, 402.1 sq. in. area, 48% amalgam holdup

$$\left(\frac{402.1}{144}\right)(50)(.48) = 67.02 \text{ cu ft}$$

Surge tanks - (30 sec holdup)

$$(61.7 \text{ gpm})\left(\frac{30}{60}\right)(2) = 61.7 \text{ gal} = 8.25 \text{ cu ft}$$

Lines - 300 ft of 3 1/2 inch line (estimated)

$$\left(\frac{9.89 \text{ in}^2}{144}\right)(300) = 20.60 \text{ cu ft}$$

150 ft of 3/4 inch line

$$\left(\frac{0.533}{144}\right)(150) = 0.55 \text{ cu ft}$$

Amalgam and storage tanks:

25 gallons/7.481 = 3.34 cu ft

Heat exchangers: (estimated)

counter current heater
400 5/8" tubes 12 ft long = 7.25 cu ft

steam heater
20 5/8" tubes 6 ft long = 0.18 cu ft

counter current cooler
400 5/8" tubes 12 ft long = 7.25 cu ft

cooler
60 5/8" tubes 12 ft long = 1.09 cu ft

TOTAL CUBIC FEET = 130.89 = 111,256.5 lbs ✓

[redacted]
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TEST FACILITY COLUMNS

Columns

Columns - 50 ft high - 28.89 sq in area, 48% amalgam holdup

$$\left(\frac{28.89}{144}\right)(50)(5)(0.48) = 24.07 \text{ cu ft}$$

Surge tanks (30 sec holdup)

$$(4.50)\left(\frac{30}{60}\right)(5)(1/7.48) = 1.50 \text{ cu ft}$$

Product End Reflux

Mixer - settlers (10 minute total holdup)

$$(4.50)(10)(1/7.48) = 6.02 \text{ cu ft}$$

Decomposers

2 cu ft (estimated) = 2.00 cu ft

Storage (135 gal tank run 1/2 full)

$$\frac{135}{2}\ (1/7.48) = 9.02 \text{ cu ft}$$

Clean-up (estimated)

1 cu ft = 1.00 cu ft

Waste End Reflux

Contactor - 3-60 gal mixers 1/3 full, 3-10 gall settlers 1/3 full

$$(3)(60)(1/3)(1/7.48) + 3(10)(1/3)(1/7.48) = 9.36 \text{ cu ft}$$

Dissolver - 270 gallons - run full

$$270/7.48 = 36.10 \text{ cu ft}$$

Decanter - 5 gal (estimated)

$$5/7.48 = .67 \text{ cu ft}$$

Surge tank - 10 gal (estimated)

$$10/7.48 = 1.34 \text{ cu ft}$$

[redacted]

[redacted]

Heat Exchanger (estimated)	= 0.18 cu ft
Lines (estimated at 15% of Total)	= 16.10 cu ft
TOTAL	= 107.36 cu ft
	= 91,256 lbs ✓

[redacted]

X-426 (Revised 1-52)

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ORNL
CENTRAL FILES NUMBER
52-10-84

DATE: October 10, 1952

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SUBJECT: CHEMICAL TECHNOLOGY DIVISION
MERCURY REQUIREMENTS FOR OREX PROGRAM

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TO: G. H. Clewett, Y-12

FROM: R. P. Milford

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OAK RIDGE NATIONAL LABORATORY

October 10, 1952

TO: G. H. Clewett, Y-12

FROM: R. P. Milford

SUBJECT: Chemical Technology Division Mercury Requirements for Orex Program

This memo will confirm our telephone conversation of today's date on the above subject.

Listed below is a summary of our mercury supply and foreseeable estimated requirements:

24-inch Column Set	800 gal	90,500 lb
Pilot Plant (Test Facility 4501)	250 gal	28,200 lb
UNOP Experimental	500 gal	57,800 lb
		176,500 lb
Less UNOP Supply	500 gal	57,800 lb
ESTIMATED REQUIREMENTS		118,700 lb

R. P. Milford

R. P. Milford
Process Design Section
Chemical Technology Division

RPM:mep
CC: F. L. Steahly
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ORNL
CENTRAL FILES NUMBER
53-1-320

DATE:	January 24, 1953
SUBJECT:	OREX Planning Committee Meeting - January 22, 1953
TO:	F. L. Steahly
FROM:	R. B. Lindauer

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The regular bi-monthly meeting of the GREX Planning Committee was held in the conference room of Building 9733-1 on January 22, 1953. The following members and visitors were present:

Committee	Visitors
T. A. Arehart	G. H. Clewett
R. E. Blanco	I. B. Cutler
W. L. Carter	D. N. Hess
J. S. Drury	
H. H. Garretson	
W. N. Johnson	
R. B. Lindauer	
D. J. Oriolo	
A. D. Ryon	

1.0 Discussion

1.1 Scouting runs on a one column azeotropic distillation system indicate adequate drying of PDA can be obtained by this method. With a column only several feet long the moisture content was reduced to 0.1%.

1.2 A PDA batch dryer having a capacity of 125 gallons per day using calcium carbide is being constructed.

1.3 Equipment for the production of $MgCl_2 \cdot 3$ PDA will be installed to provide slurry for the testing of centrifuges and filters. Preliminary tests indicate a nylon filter may be suitable at rates of 20 GPH/sq. ft. Filtration has the advantage in ease of washing of lithium from the cake.

1.4 Tests using tetrahydrofuran as solvent in the seven-end reflux showed only 4% inversion. The ten-fold lower solubility of sodium chloride in THF compared with PDA also indicates a much slower six-end reaction.

1.5 The advantages and disadvantages of the $MgCl_2 \cdot 3$ PDA chemical desolvation methods being studied were discussed.

1.6 The desolvation limit using the 2-ethyl hexanol high boiler method seems to be approximately 0.25 moles of PDA per mole of magnesium. This PDA loss is too large considering the limited supply of PDA.

53-1-320

Hg = $2.56/lb
See CF-54-8-42

1.0 Discussion (continued)

1.7 The minimum amount of mercury carried with the amine stream from the 7-end Rushton columns has been 0.7 grams/liter up to the present time. This would correspond to a loss of $200.00 of mercury per day in the test facility. It is believed that smooth operation will lower this loss substantially.

1.8 A visit to New York was made to obtain information on magnesium and PDA. The cost of ground magnesium will be between 32-1/2 and 56-1/2 ¢ / lb. depending on the source. No information could be obtained on disposal of magnesium from the plant. The maximum production rate of Carbide and Carbon for PDA is sufficient to supply the OREX test facility and they will accept an order for 164,000 lbs/year. A full scale OREX plant will require construction of new PDA production facilities.

1.9 Economic studies on the various desolvation methods are still in progress.

2.0 Recommendations

2.1 A dry nitrogen gas blanket should be used in the OREX test facility unless future work shows this system to be unsatisfactory.

2.2 Since existing data does not clearly indicate the superiority of any one of the desolvation methods currently being investigated, no decision will be made on the selection of a method for at least two weeks.

The meeting was adjourned at 11:00 AM. The next meeting will be held in the conference room of Building 9733-1 on Thursday, February 5, 1953 at 8:00 AM.

R. B. Lindauer

R. B. Lindauer

RBL:aeh

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OAK RIDGE Y-12 PLANT INFORMATION CONTROL FORM

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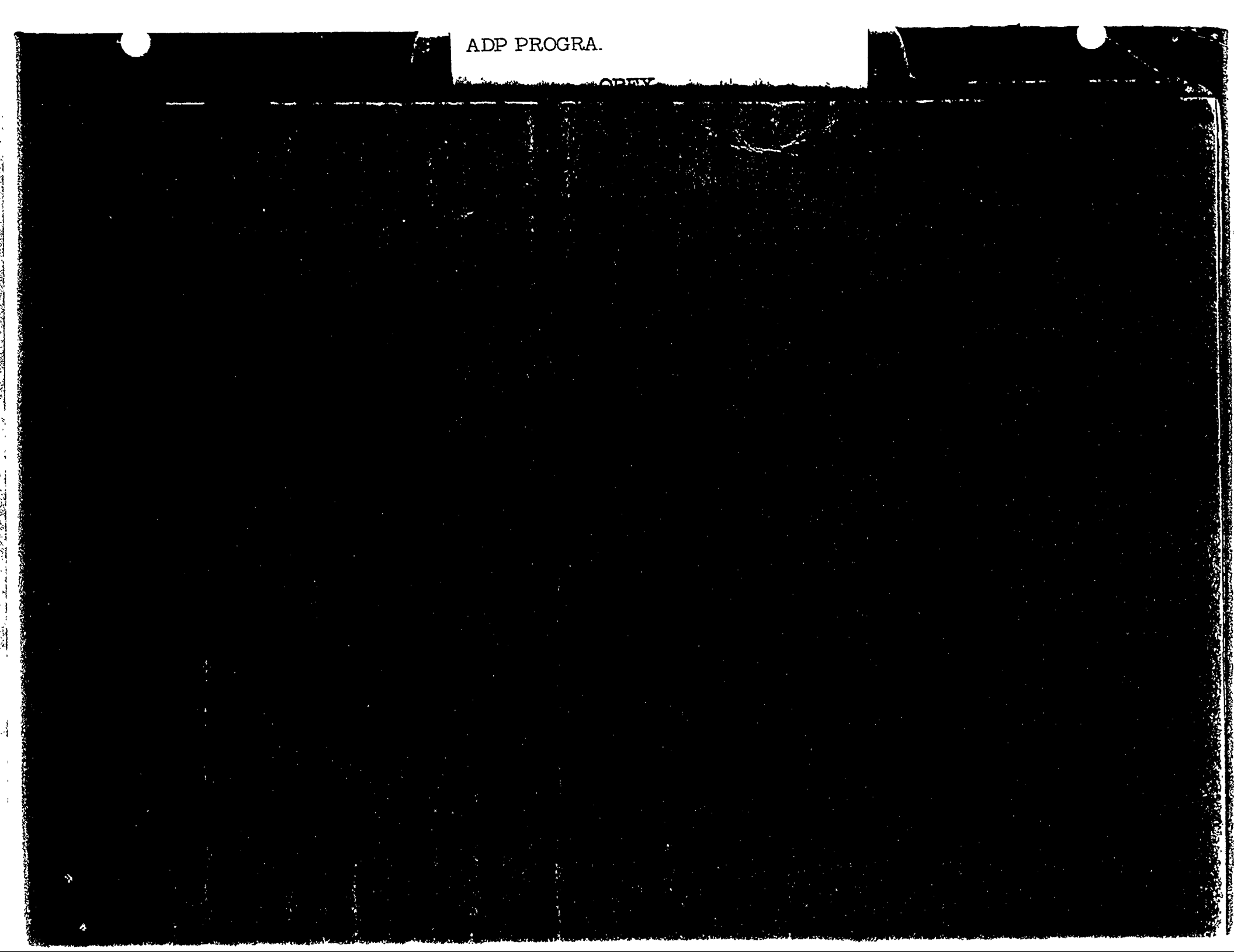

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TO: Mr. J. M. Case

SUBJECT: Starting of CRIL Pilot Plant Operations

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File (WHM) I-12RC

Plans are now made for the CRIL Research group to start operations on a 3-shift basis in the CRIL pilot plant April 13. PDA drying operations will be started on this date. Solvent and other process solutions and materials will be introduced in the plant within the following week or ten days as systems are completed and released for operations. This notice is prepared for the purpose of informing the Maintenance Division concerning the schedules as well as some of the suggested procedures in order to reduce safety and fire hazards which exist in this building. When operations are started the following rules will apply in the CRIL pilot plant area:

1. Smoking - No smoking will be permitted in any process area including all floors, penthouse, and roof. Also no smoking will be allowed near the carbide waste tank on the north side of the building. These areas will be posted with "No Smoking" signs. Smoking will be permitted in the third floor office, change rooms, toilets, stairway between third floor and acid room, main north-south corridor on first floor, maintenance shops and areas outside of the building except as noted above.

2. Eating - No food, drink or tobacco will be allowed in the pilot plant process areas (same as No Smoking areas).

3. Clothing - Recommendations have been made by the Health Physics Department that fresh clothes be worn each day by all maintenance people who must work in process areas.

Safety and First Aid procedures relative to hazards encountered in the operation of this plant are being prepared by the Safety Department in conjunction with the Health Physics Department. The Safety and Fire Departments will assume the responsibility of acquanting all maintenance personnel with the safety and fire hazards peculiar to the operation and the uses of necessary protective equipment.

During the time from the beginning of operation of this plant until the plant is in full operation, a considerable number of maintenance personnel will be working in process areas on the day shift. We realize that certain hazards exist whereby it is possible that these people may perform some operation on piping or equipment which may be filled with process solutions. In order to avoid the possibility of accidents, we are requesting that no process lines be cut or in any way opened without the specific approval of the field engineer, Mr. F. V. Stanfel, who will have double checked with the operating foreman in charge before issuing any instructions or opening any line or vessel. It must be pointed out that extreme care and the greatest cooperation must be exercised by all concerned in order to avoid accidents and or serious operation delays due to mistakes during the period of time when operations startup is in progress along with the completing of the installation of this plant.

W. L. Morgan

/DD:ys

X-426 (Revised 1-52)

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58-6-122

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SUBJECT: START-UP PROCEDURE FOR THE OREX TEST FACILITY

TO: H. E. Goeller

FROM: H. O. Weeren

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OAK RIDGE NATIONAL LABORATORY

TO: H. E. Goeller DATE: June 15, 1953

FROM: H. O. Weeren

SUBJECT: START-UP PROCEDURE FOR THE OREX TEST FACILITY

This report presents in simplified form the start-up procedure that has been proposed for the Test Facility. This procedure was agreed upon after numerous conferences with pilot plant and Unit Operations personnel and includes the suggestions of many of those concerned.

This procedure is intended for the original start-up only and is not intended for subsequent start-up after shutdown; other procedures will be devised for these cases.

It has been assumed for this start-up procedure that the system has been completely purged before start-up begins and that this start-up procedure commences with the system dry and filled with nitrogen.

H. O. Weeren

H. O. Weeren
Process Design Section
Chemical Technology Division

HOW:amh

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T. D. Kahn 9/3/71

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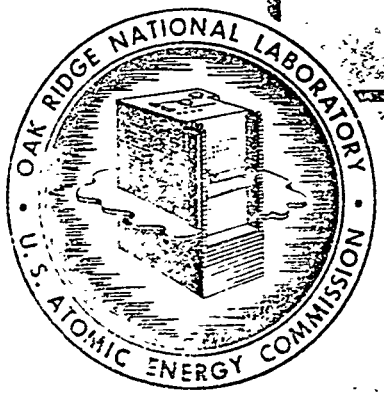
OREX TEST FACILITY
OPERATING MANUAL



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OPERATING MANUAL

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FROM: R. B. Lindauer

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Mary Lynn Cameron

OREX TEST FACILITY OPERATING MANUAL

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CHAPTER I - FIGURES continued

CHAPTER I - FIGURES continued

TABLES

CHAPTER I - TABLES continued

CHAPTER II

FIGURES

CHAPTER II - FIGURES

TABLES

CHAPTER III

FIGURES

TABLE 3.12

SOLUBILITY OF LITHIUM IN MERCURY (32)

Temperature °C	Weight % Li	Moles Li/liter Hg at 25° C
0	0.023	0.45
20	0.041	0.80
40	0.065	1.27
60	0.093	1.82
80	0.125	2.44
100	0.155	3.03

TABLE 3.13

SPECIFIC GRAVITY OF AMALGAMS (33)

Metal	% Weight	Specific Gravity
Li	0.0301	13.500
	0.503	13.135
	2.166	10.925
Na	0.103	13.448
	0.597	12.965
	2.631	11.701
K	0.184	13.371
	0.950	12.908

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TABLE 4.2

AMALGAMAKER TANK LIST

T. M. No.[a]	Capacity (gals)	Use
[illegible]-A	1	Baffle tank to maintain heel in decomposer
[illegible]-B	10	Surge from decomposer to acid wash column
[illegible]31	685	Potassium amalgam storage
[illegible]505	150	Store used amalgam prior to decomposition
[illegible]506	150	Clean mercury storage for feed to amalgamaker
[illegible]507	15	Surge in amalgam line from amalgamaker to storage
[illegible]508	60	KOH dissolver and feed tank for amalgamaker
[illegible]512	150	Lithium amalgam storage
[illegible]5	60	LiOH dissolver and feed tank for amalgamaker
[illegible]527	10	Mercury surge from clean up column to clean mercury tank
[illegible]536	15	Tank for mixing HNO_3 for flushing equipment and lines when changing to production of different amalgam

(a) All tanks except CR-531 are constructed from stainless steel. CR-531 is constructed from carbon steel.

3.0 OPERATING INSTRUCTIONS

These instructions are written before fabrication and installation of the piping and will need to be revised when the piping is actually installed. Since this installation is entirely for the purpose of obtaining information, great flexibility in operations will be necessary. At the present time it is possible to get the desired information with two general equipment arrangements; (1) operation with the cold column alone for determining flooding capacities and holdup over a wide range of pulse amplitude and frequencies (2) operation with both the hot column and the cold column to get stage height data over a limited range of pulse amplitudes, pulse frequencies and volume velocities. Separate operating instructions have been written for each of these conditions.

3.1 Process Flow for Flooding and Holdup Tests

LiCl(PDA), 0.8 M with respect to lithium, made in the closed reflux facility is unloaded from transport vessel DTC-515 into the solvent surge and storage tank DTC-510 which is maintained at 30°C. The cold column is filled with amine by two solvent pumps in parallel, an Aerojet turbine pump and a Viking rotary pump. The amine phase enters the pulse leg of the pulse generator near the base of the column, flows through the column, leaving the top to re-enter the solvent storage tank. The Aerojet pump delivers at a given capacity, the flow control being through the Viking rotary pump, the orifice being located in the amine line from the top of the column to the solvent storage tank. In cold weather operation, amine is recirculated from the storage vessel through the cold column until the temperature of the amine in the column reaches 35°C before amalgam is pumped to the column.

Potassium-lithium amalgam, 0.7 M with respect to lithium and 0.4 M with respect to potassium, also prepared in the closed reflux facility is transferred from a transport vessel into the amalgam storage and surge tank DTC-549. Two Johnston turbine pumps (DTC-400 and DTC-402) are paralleled and pump the amalgam phase from the storage tank to the top of the column. The amalgam phase pumped by DTC-402 is maintained at a constant flow rate, the flow controller regulating

The shift supervisor at the CR facility should be notified to load solvent. It will require around 20 trips to load DTC-510. Load transport vessel DTC-515 with as near to 150 gallons of solvent as possible from tank CR-567 using pump CR-1408 and bring to the DTC facility by truck. Remove from truck by crane.

Position DTC-515 above DTC-510.
Make connection between vessels
Open valve to vent DTC-515.
Open valve 101.
Open valve on DTC-515.
When DTC-515 is empty, close valve 101 and valve on DTC-515.
Break connection.
Record on forms "Solvent Charging" the data requested.
(Sight glass reading, trip number, date, time, operator name, etc.)

Transfer of Amalgam from Closed Reflux System to Solvent Storage Vessel DTC-54

Transport vessel DTC-515 will also be used to bring amalgam to the DTC equipment from the CR plant. Only 100 gallons of amalgam will be loaded at a time into the 150 gallon container since 100 gallons weighs 11,000 pounds. The transport vessel will be carried by truck to the CR facility, loaded to 100 gallons (measuring device not yet certain), brought to the DTC facility, picked up by crane from the truck and emptied into amalgam storage tank DTC-549. About 600 gallons of amalgam will be required.

Startup Procedure for Flooding Studies

The cold column process flow for flooding studies was outlined in Section 3.2. It is assumed that solvent storage tank DTC-510 is filled with around 3000 gallons of solvent and that amalgam storage tank DTC-549 contains around 600 gallons of amalgam.

Valve Check List for Startup in Flooding Studies

X-closed 0-open

V. No.			V. No.			V. No.		
1	X		72	X		24	X	
2	X		8		0	23	X	
3	X		9		0	91	X	
4		0	10		0	27		0
5	X		11	X		28	X	
89	X		51		0	29	X	
76	X		50	X		30		0
6		0	90	X		31	X	
7		0	25	X		33	X	
87	X		26	X		77	0	
81	X		13	X		12		0

Startup Procedure for Flooding Studies

The cold column process flow for flooding studies was outlined in Section 3.2. It is assumed that solvent storage tank DTC-510 is filled with around 3000 gallons of solvent and that amalgam storage tank DTC-549 contains around 600 gallons of amalgam.

Valve Check List for Startup in Flooding Studies

X-closed O-open

V. No.			V. No.			V. No.		
1	X		72	X		24	X	
2	X		8		0	23	X	
3	X		9		0	91	X	
4		0	10		0	27		0
5	X		11	X		28	X	
89	X		51		0	29	X	
76	X		50	X		30		0
6		0	90	X		31	X	
7		0	25	X		33	X	
87	X		26	X		77	0	
81	X		13	X		12		0

Draining Amine Lines

Check that valves 102, 123, 147 and 148 and 157 are closed.

Check that valves 120, 122, 159 are open.

When level recorder, 307 DTC shows no more build up, put FCV-304-DTC on manual air and in open position.

Check that valves 111, 153, 153, 106, 155, 104, 103, 137, 55, 101 are closed.

Check that valves 117, 112, 113, 114, 115, 108, 109, 110, 107, 151, 153, 156, 151, 54 are open.

Start Lapp Pulsafeeder and pump until level recorder LR-307 DTC shows no increase in buildup.

Shut off Lapp Pulsafeeder and drain.

Draining Water Lines

Let temp. controller TCV-301 DTC on manual instrument air and in open position.

Open valves 304, 305, 306, 307, 443, 441.

3.4 Operating Instructions for HETS Studies

At the conclusion of the flooding studies, a series of tests to determine the effect of pulse amplitude, pulse frequency and volume velocity upon the efficiency of the isotopic separation (or the height equivalent to a theoretical stage). The process flow for this normal operation is given in Section 3.3 The molarities of lithium in mercury and PDA will be checked at this point and brought to their proper values by additions from the CR system. If transfer of amalgam or amine is required, follow the procedure listed in Section 3.5. This set of instructions assumes around 3000 gallons of amine in solvent

storage tank DTC-510 and about 600 gallons of amalgam in DTC-549.

Valve Check List for Startup from Empty System for Normal Operation

X-closed

0-open

V. No.			V. No.			V. No.		
101	X		14	X		124		0
159		0	15	X		149		0
102	X		16	X		125	X	
137	X		17	X		126	X	
153	X		18	X		127		0
103	X		19	X		128		0
151	X		20	X		129		0
104		0	93		0	152	X	
106	X		119		0	130		0
107		0	79	X		132	X	
155	X		80	X		133		0
108		0	81	X		134	X	
109		0	13	X		163	X	
110	X		12		0	162	X	
111	X		120		0	135		0
112		0	121	X		86	X	
117		0	122	X		136	X	
116	X		123		0	22	X	

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TO: L. B. Emlet

FROM: G. H. Clewett

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DATE December 7, 1953

COPY TO C. E. Larson
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C. E. Winters
F. L. Culler

SUBJECT Review of the Purpose and Status of the Orex Development Program as of December 7, 1953

As requested, I have prepared the following brief review of the purpose and status of the Orex Development Program (as of this date) for your use during the course of General Nichols' impending visit.

In the initial survey by this division of chemical methods of separating lithium isotopes, it was recognized that a stable system composed of lithium amalgam and organic solvent should satisfy the requirements for a suitable system. This conclusion was based upon the moderate success achieved by Lewis and McDonald (published in 1936 in J.A.C.S.) using lithium amalgam versus solutions of a lithium salt in alcohol and dioxane. The side reactions and emulsion troubles encountered by Lewis and McDonald prevent exploitation of their system for large scale production. The inherent possibilities, however, were recognized as being great enough to warrant a determined search for a solvent free of reaction or emulsion effects in contact with amalgam. While searching for such a solvent and for reflux processes for a system of this kind, studies were carried out on the electrolysis of aqueous lithium hydroxide to form amalgam which led to the concept of the Elex process and finally resulted in the β-4 plant. However, in all of this early work the ever present reaction of amalgam with the water phase seemed to be a serious drawback which could best be surmounted by developing a non aqueous system completely free of inter phase reaction. The discovery, at this time, that propylene diamine provided a reaction-free system seemed to offer hope for the development of a near perfect system. Accordingly, two main development

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programs ensued. (1) Improvement work on the aqueous system by the production groups who by this time were charged with operating and improving the Elex plant. (2) Exploitation by ORNL of the organic system which surmounted the difficulty of reaction between phases.

The first of these main programs is characterized by the following. The large scale pilot plant work disclosed that in a clean system lithium amalgam is much more stable than the early bench scale work indicated. Further, it was found that if the electrodes were removed, the consequent freedom from oxygen gas imparted sufficient stability to allow extensive countercurrent contacting without undue decomposition. These properties have been exploited in the process now known as Colex.

The second major program mentioned above, that concerned with the organic system, was labeled Orex and can be characterized as follows. The freedom from interphase reaction has indeed been of advantage and it imparts a tremendous flexibility to the system. This flexibility has resulted in the development of a true closed cycle system, which is the ultimate goal in all chemical exchange isotope separation schemes wherein all chemicals used at one end of the system are obtained as waste from the other end. In fact, the flexibility inherent in the system has allowed for the development of more than one such ideal closed cycle process.

The entire process may be described as follows: The main exchange section involves the countercurrent contacting of lithium amalgam with a solution of lithium chloride in propylene diamine. Reflux at the product end is obtained by contacting the lithium amalgam with a slurry of sodium or potassium chloride in P.D.A. in a manner as to cause the following reaction to take place:

$$\left.\begin{matrix} NaCl \\ \text{or } KCl \end{matrix}\right\} + Li\ (\text{amalgam}) \longrightarrow \left.\begin{matrix} Na \\ \text{or } K \end{matrix}\right\} \text{amalgam} + LiCl$$

The lithium amalgam is reformed at the other end of the system by reversing the above reaction by suitable adjustment of temperature, concentration and other factors.

As of this writing, the Orex process cannot be said to be a proven, completely demonstrated process although all the separate operations which go to make up the whole process have been repeatedly demonstrated successfully. The Y-12 pilot plant has

served to demonstrate that moisture in the system is difficult to eliminate completely and when present causes a serious product removal at the product end in the form of insoluble lithium hydroxide. This appears to be the only major deterrent to success at the present time. Measures are being taken to eliminate this problem which have every indication of being successful. Further work at the Y-12 pilot plant and at the X-10 Orex test facility will undoubtedly lead to demonstration of the technical feasibility of the process. Cost studies in the past have shown repeatedly that Colex and Orex are competitive economically so that successful production of product level material by Orex will certainly point up the importance of cost studies current at that time.

A tabulated comparison of the two processes as they appear to this writer at this time follows in the attached tables.

G. H. Clewett

[redacted]

	COLEX		OREX	
	Advantages	Disadvantages	Advantages	Disadvantages
Exchange Section	No blanket gas needed. Hydrogen evolved adequately blankets the system but must be disposed of.	Troublesome pump problems. Inflexible with regard to type of contactors which can be used.	Can be run in any type columns or contactors - whatever is cheapest. Pumping is relatively trouble free.	Blanket gas needed.
Product end reflux	One of the simplest and most trouble free refluxes found in any chemical exchange system. This is of great importance and cannot be discounted.	Must be designed properly to allow impurities to bleed out and yet not lose too much product.	The chemical energy represented by alkali metal amalgam is not lost in the reflux.	Very sensitive to traces of moisture and oxygen which can lead to inefficiency in cascade performance.
Waste end reflux	Simple in principle despite its size.	Large and costly to build and operate.	Capable of achieving savings in electrical (or equivalent chemical) power. Potentially a smaller installation.	Possibly more complex than Colex.

[redacted]

[redacted]

	COLEX		OREX	
	Advantages	Disadvantages	Advantages	Disadvantages
Auxiliaries	Less numerous than Orex	Limited number of structural materials can be used. Refrigeration required.	Refrigeration not required. Corrosion is less of a problem.	More numerous than Colex - some not found in Colex - drying still-blanket gas system etc.
General	Simple process in general. Important principles have been well demonstrated insuring technical feasibility.	Inflexible - Amalgam production would appear to be an ever present costly necessity. Sensitive to impurities. Pumping problems may be difficult to eliminate entirely. Decomposition reaction ever present limiting flexible cascade design. Very large mercury inventory required.	Extremely flexible with great range for extensive improvements and simplification. Insensitive to impurities (except water and oxygen). Less mercury inventory. Wide temperature range possible so that operation at the optimum is possible.	Has not been completely demonstrated as yet, although all the separate operations have been repeatedly demonstrated. More complex than Colex requiring a wider range of separate types of chemical engineering equipment, all standard equipment however.

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DTC Installation

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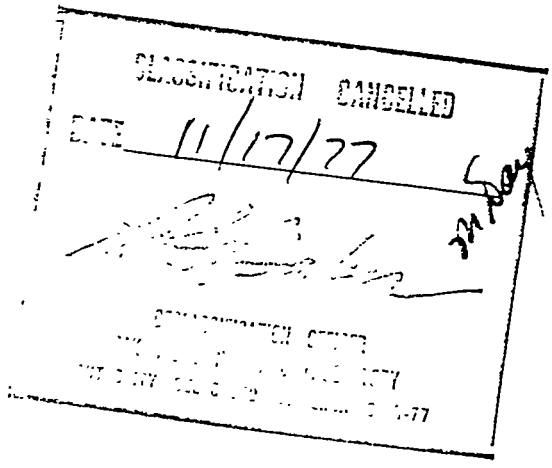

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ACKNOWLEDGMENTS

The basic process information for the design of the Large Column Set was obtained almost entirely from research and pilot plant data obtained by the Materials Chemistry Division during the fall of 1952 and early months of 1953. The engineering and design of the specialized equipment, i.e., the columns and pulse generators, were handled by the Special Equipment Design Group of the Engineering Department with assistance and advice on certain phases by members of the Catalytic Construction Company. Design, procurement, and supervision of the instrumentation were functions of the Instrument Division. The piping and vessel drawings and sketches were prepared by the cooperative efforts of both Catalytic and ORNL designers and draftsmen. Catalytic was largely responsible for structural engineering design and assisted in the procurement of many items of equipment. Construction and installation of the facility were handled by the Mechanical Department of the Engineering and Mechanical Division.

The excellent cooperation received from Catalytic personnel and the integration of Catalytic and Carbide personnel into an efficiently functioning organization are worthy of special commendation. Praise is also extended to the members of the Engineering and Mechanical Division, through whose tireless efforts the construction schedule was met.

1.0 ABSTRACT

A summary of the engineering data and description of equipment for the design and erection of an Orex large scale test loop at Oak Ridge National Laboratory is presented. The set was constructed primarily to obtain scale-up data for the transition from pilot plant to full scale plant design.

The Large Column Set is based on the Dual Temperature system for the separation of the isotopes of lithium.

2.0 INTRODUCTION

2.1 Scope of Report

This report follows the same general form as the Project Engineering Report for the Orex Test Facility (CF-53-12-161).

The engineering data and design criteria utilized for the procurement and installation of the Large Column Set are presented in abbreviated form. The more important reasons for the design and selection of equipment are included to aid the reader in understanding the final installation. Information contained in this report should be useful for full-scale plant design or to personnel contemplating the use of similar equipment for other processes.

2.2 Description of the Facility

The Large Column Set is basically an engineering test loop built to obtain scale-up data for Orex plant design.

The design is based on a process known as the Dual Temperature system. This process employs a series of pairs of thermally hot and cold columns to effect the separation of the two stable isotopes of lithium. It is similar to the Chemical Reflux process in that countercurrent streams of lithium amalgam and lithium chloride solution in propylenediamine (PDA) are contacted in exchange columns. Under these conditions the Li^6 isotope tends to concentrate in the amalgam phase and the Li^7 isotope in the amine phase. Advantage is taken of the variation with temperature of the separation factor, which factor is approximately 1.051 at 26°C and 1.028 at 99°C. In contrast to the Chemical Reflux process where the reflux of the streams is handled by chemical recombination and return to the columns, the Dual Temperature system permits the concentration of Li^6 in the amalgam at the low temperature and the return to the amine phase at the higher temperature in each pair of columns. Although the Dual Temperature system is basically simpler, it has the disadvantage of a considerably lower overall separation factor, approximately 1.01, then the Chemical Reflux process.

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FROM: C. E. Larson

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POST OFFICE BOX P
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August 3, 1954

United States Atomic Energy Commission
Oak Ridge Operations
Post Office Box E
Oak Ridge, Tennessee

Attention: Dr. Herman M. Roth, Director, Research and Medicine

Subject: TERMINATION OF THE OREX PROJECT

Gentlemen:

Development effort on the Orex process for the ADP separations was discontinued during the first two weeks of July, 1954, as scheduled. The operation of the Component Test Facility terminated on July 15, 1954; operation of the Dual Temperature Columns was terminated during April, 1954. All Orex development costs have been accumulated in the FY 1953 and FY 1954 budgets with the exception of $330,000 to be expended during FY 1955 for reporting, mercury purification, and equipment dismantling. In FY 1955, mercury worth approximately $700,000 will be returned to production channels for credit. These charges have been indicated in the ORNL budget request for FY 1955 and in CF No. 54-7-149 (letter from C. E. Larson to H. M. Roth, dated July 19, 1954, subject: Revisions to 2000 Program Activities for ORNL for FY 1955 and FY 1956).

Report preparation, plant and equipment clean-up, and mercury recovery will require approximately eight man-years and $230,000. An additional $100,000 has been requested to cover costs for the dismantling and salvage of the Orex equipment in the Component Test Facility, the Dual Temperature Columns and possibly in the Orex Pilot Plant.

4-12?

[redacted]

[redacted]

Orex equipment and instruments will be made available to all groups in the Laboratory for use in projects currently in progress. A priority system will be established under which those groups most urgently needing new equipment will have an opportunity to secure material from the Orex project. After all priority demands have been satisfied, the equipment will be made generally available.

Very truly yours,

OAK RIDGE NATIONAL LABORATORY

M. E. Ramsey
for C. E. Larson
Director

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Oak Ridge Operations Office

FROM: C. E. Larson

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January 10, 1955

United States Atomic Energy Commission
P. O. Box E
Oak Ridge, Tennessee

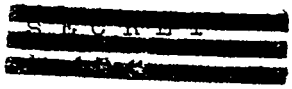
Attention: Dr. H. M. Roth, Director, Research and Medicine Division, Oak Ridge Operations Office

Subject: PROPOSAL FOR A NEW PROGRAM - METALLEX

Gentlemen:

During FY-1954 and FY-1955 work was carried out at ORNL on the Metallex process, a promising method for producing thorium metal. It is requested that the level of activity on Metallex process development be increased from the present study of the reduction step to a more intensive investigation of all of the process steps. We request that this investigation be carried out under a new 2000 program, Metallex, with budgets of 3.0 man-years and $95,000 in FY-1955 and 6.5 man-years and $351,000 in FY-1956. Metallex development was formerly carried as a part of the 5000 program Feed Materials Processing. Manpower for the program will be made available by reduction in the 5000 programs; Hope, Thorex, and Volatility Studies in FY-1955; and reduction in the Excer and Feed Materials Processing programs in FY-1956. The considerations which prompt this request follow.

In FY-1954 the ORNL initiated research and development on Feed Materials Processing. During the program it became apparent that existing thorium metal production methods should be amenable to improvements which would result in significant economies. The present thorium production process is inherently expensive because of the costly reductant, calcium, which is employed and because of the necessity of an expensive remelting operation. During FY-1954 a search was initiated at ORNL for a thorium reduction process which would avoid these costly steps and yield inexpensive thorium metal. As a result of this program the Metallex Process has evolved. The Metallex Process employs sodium amalgam to reduce thorium tetrachloride to a thorium amalgam. Mercury is subsequently separated from thorium by filtration, cold pressing and,



finally, vacuum retorting at 1100°C. Experimental gram batches of the resulting metal have had approximately 90% of the theoretical density of cast metal, and have had a Brinell hardness of only 30 after cold working and annealing. Therefore, it is probable that thorium rods may be made by simple extrusion of the metal after retorting. On the basis of laboratory data, thorium produced by the Metallex Process promises to meet all specifications for reactor grade metal.

Comparative cost estimates have been made of the Metallex process, the existing thorium metal production process, and an alternate electrolytic method which is now being pilot planted. We conclude that the Metallex process will produce thorium metal for less than $2.00 per pound, including amortization, a cost well below that of the other processes.

Although the Metallex process is still in the laboratory stage of development, we believe that it shows sufficient promise to be considered seriously for thorium metal production. We recommend that consideration be given to pilot planting the Metallex process before the process selection date for contemplated expansion in thorium metal production.

The enclosed memorandum reviews in more detail the status of the Metallex process.

Very truly yours,

OAK RIDGE NATIONAL LABORATORY

C. E. Larson

C. E. Larson
Director

CEL:FLC/g

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CONTENTS

1.0 INTRODUCTION

In FY 1954 work was initiated at the Oak Ridge National Laboratory on more economical methods for preparing uranium and thorium metal from their compounds. At the inception of the program criteria were established for processes which should achieve marked economy over existing methods. These were: continuous processing rather than batch; low temperature reduction; use of an inexpensive reductant; and elimination of remelting. Of the many reactions that were investigated, the reduction of uranium tetrachloride with sodium amalgam met most of these criteria and appeared most promising. The same chemistry was also found feasible for the reduction of thorium, and emphasis was shifted to this metal because of the need for increased production capacity. The process employing sodium amalgam for the reduction of uranium and thorium tetrachlorides has been named the Metallex process.

Until recently the reduction reaction was carried out between sodium amalgam and the metal chlorides which were dissolved in anhydrous propylenediamine. It has been found, however, that the reduction occurs equally well when the solid tetrachlorides are added directly to sodium amalgam. Although only a limited number of runs have been made without propylenediamine, the product appears comparable in purity and density to that obtained when propylenediamine is used. Therefore, in this discussion the Metallex process reacts solid tetrachloride with sodium amalgam directly. If it should subsequently be found that propylenediamine is necessary, the cost of thorium produced by Metallex process would not be significantly increased.

2.0 SUMMARY

The Metallex process is a new method for producing metallic uranium and thorium. The process for producing thorium consists of the following steps (Figure 1):

1. Aqueous thorium nitrate is evaporated to molten salt and subsequently denitrated to thorium oxide.

2. Thorium oxide is reacted with carbon at 2000°C to form thorium carbide.

3. Thorium carbide is chlorinated with chlorine gas at 400°C to form thorium tetrachloride.

4. Thorium tetrachloride is reacted with 4 M sodium amalgam at 100 to 160°C to form an amalgam containing one weight per cent thorium.

5. The amalgam is washed with water and 1 M hydrochloric acid to remove sodium and sodium chloride.

6. The thorium concentration of the amalgam is increased to eight weight per cent by filtration, and to 16 weight per cent by cold pressing at 20,000 psi in a steel die to yield a solid cylinder.

7. The solid amalgam cylinders are retorted at 1100°C and $<$ 0.1 micron pressure for one half to two hours to remove mercury. It is significant to note that massive thorium metal is produced by this process at a temperature 700°C below its melting point.

8. The sintered cylinders, in an inert atmosphere, will be compressed into a billet and extruded to form rods suitable for slug fabrication. This step of the process has not yet been demonstrated, but the measured physical properties of the Metallex product indicate its feasibility.

Typical analytical data on Metallex product show the major contaminants to be: mercury, 13-40 ppm; carbon, $<$ 300 ppm; nitrogen, $<$ 200 ppm; and

oxygen, ~ 2000 ppm. Cold worked Metallex thorium had a Brinell hardness of about 60. After annealing the hardness was 30.

A preliminary cost estimate was made of a 1000 ton per year Metallex plant for converting thorium nitrate to thorium metal billets. The indicated production cost was less than $2.00 per pound of thorium including amortization. The total plant investment was $6,980,000, and the annual operating cost was $1,618,000. Comparative cost estimates of thorium production processes indicate that Metallex promises to be the most economical of those proposed.

3.0 PREPARATION OF THORIUM TETRACHLORIDE

Several methods for preparing thorium tetrachloride from thorium nitrate have been evaluated on a small scale. The common starting material for thorium tetrachloride is thorium oxide. Thorium oxide may be prepared by thermal decomposition of thorium nitrate or by thermal decomposition of thorium oxalate. Both of these methods for preparing thorium oxide have been well-explored and will not be considered further. The conversion of thorium oxide to thorium tetrachloride may be accomplished by several methods.

3.1 Carburization - Chlorination of Thorium Oxide

Thorium oxide may be reacted with carbon at 2000°C to form thorium carbide. This reaction is readily carried out in an electric furnace similar to that employed for the commercial production to carborundum (silicon carbide). The resultant thorium carbide reacts readily with chlorine at 400°C. The reaction rate of thorium carbide with chlorine at 400°C is approximately 30-fold greater than the rate of reaction of thorium

oxide-carbon mixtures at 500°C. Consequently, the carburization step minimizes the exposure of process equipment to the highly corrosive chlorine atmosphere. The carburization-chlorination reaction results in approximately 99% conversion of the oxide to tetrachloride. This procedure involves conventional techniques and is therefore proposed for the Metallex process. With development, however, the direct denitration-chlorination reaction which will be subsequently described promises to be superior.

3.2 Simultaneous Thorium Nitrate Denitration-Chlorination in a Flame Reactor

It has been found that thorium nitrate--carbon mixtures react rapidly with chlorine at 300-400°C. Since this method may be hazardous on a batch basis, efforts are being directed toward the development of a continuous flame reactor having only a small quantity of reactants in the reaction zone. In this case the reaction may take place in one step by the introduction of 2 M $Th(NO_3)_4$ into a hydrocarbon-oxygen-chlorine flame. Alternatively, a two-step process may be used in which 2 M $Th(NO_3)_4$ is introduced into a flame of hydrocarbon and oxygen to form thorium carbide. This mixture may be subsequently chlorinated to form thorium tetrachloride.

3.3 Direct Chlorination of Thorium Oxide

Thorium oxide-carbon mixtures may be reacted at 500°C with carbon tetrachloride-chlorine to form thorium tetrachloride. The reaction proceeds slowly, however, only about 90 per cent conversion being obtained in 4 hours. In order to obtain pure thorium tetrachloride it is necessary to sublime the products of this reaction at 800°C. This method presents many corrosion problems resulting from long contact times in chlorine atmospheres at high temperatures.

3.4 Fused Salt Chlorination

Thorium nitrate may be denitrated by heating in a molten KCl-NaCl bath, and the resulting thorium oxide chlorinated in situ with phosgene at 680°C. The product thorium tetrachloride may be leached from the solid, pulverized salt with propylenediamine after cooling. This reaction proceedes slowly, requires large excesses of phosgene, and appears to offer no advantages for preparing Metallex feed.

4.0 REDUCTION

Most of the Metallex technology has been developed with anhydrous propylenediamine as solvent for the thorium tetrachloride which is fed to the reduction step. Thorium tetrachloride dissolves readily in hot anhydrous propylenediamine to the extent of $\sim$ 0.5 M. The propylenediamine should contain less than 0.3% water to prevent hydrolysis and the precipitation of $ThOCl_2$. On contact with sodium amalgam, the thorium is reduced and transfers to the amalgam phase and sodium chloride to the propylenediamine phase,

$$ThCl_{4(PDA)} + 4Na_{(Hg)} \xrightarrow{120^{\circ}C} ThHg_{x(Hg)} + 4NaCl_{(PDA)}$$

Sodium chloride is insoluble in the organic phase and is removed by centrifugation. The clear PDA is then recycled for reuse.

Thorium has only limited solubility in mercury at 120°C and appears as a solid mercuride, $ThHg_x$, dispersed in the mercury phase. The thorium content of this phase is about 1 weight per cent when one volume of 4.0 M sodium amalgam is mixed with two volumes of 0.5 M thorium tetrachloride in propylenediamine. Sixty to 90% of the thorium present in the propylenediamine is reduced to the metal in a single one-half hour contact at 120°C. The $ThHg_x$ is recovered from the amalgam phase by

filtration on a coarse fritted disc and appears as a "cheese" containing 8 weight per cent thorium. The cheese is then washed with water and 1 M HCl to remove residual sodium and propylenediamine. The amalgam filtrate is recycled to the process through an aqueous sodium hydroxide, electrolytic amalgamator where the sodium amalgam strength is restored to 4.0 M. The thorium recycle in the filtrate is less than one per cent.

Mixer-settlers may be used to obtain the contacting required in the reduction step. Other methods, such as spray columns, are also being studied on a small scale.

Recent experiments have shown that solid thorium tetrachloride reacts equally well with sodium amalgam at temperatures of 100-160°C. The products of this reaction are thorium quasi amalgam and sodium chloride. Since sodium chloride is not wet by the amalgam, it is easily removed when the amalgam is washed with water and 1 M hydrochloric acid to remove residual sodium. The product from this reaction has been found equivalent to that obtained when propylenediamine was employed as solvent for the thorium tetrachloride. Consequently, the direct reduction of solid thorium tetrachloride with sodium amalgam is proposed in the Metallex process.

5.0 METALLURGICAL TREATMENT

The conversion of thorium amalgam to billets is being studied by the Metallurgy Division at the Oak Ridge National Laboratory.

5.1 Cold Pressing

The thorium amalgam "cheese" obtained by filtration of the quasi amalgam is cold pressed at 20,000 psi, in a steel die, to a solid cylinder containing ~16 weight per cent thorium. The press acts as a filter, the $ThHg_x$

remaining in the die and free mercury containing less than 1.0 per cent of the thorium passing through the die clearance. The cylinders which have been made to date measured about 1/2-1 in.-dia. x 1-in.-high.

5.2 Retorting

The solid amalgam cylinders are retorted at 0.1 micron pressure and 1100°C for 1/2 to 2 hours to remove mercury. During this period the cylinder shrinks to about 0.25 in. in diameter by 0.9 in. high, but retains its original geometry. Massive thorium metal with a density 80-95% that of theoretical is formed. This is an extremely important process feature in that massive metal is formed rather than a pyrophoric powder, even though the temperature employed is 700°C below the melting point of thorium. The amount of residual mercury varies with temperature and the heating time cycle employed. Heating for 1/2 hour at 1100°C reduced the mercury content to 13 ppm which is well within the tentative mercury specification of 39 ppm.* A temperature of at least 800°C has been found necessary to decompose the $ThHg_x$ compound. Further work on the thorium-mercury system is projected. Table 1 shows typical analyses of Metallex thorium after the retorting step.

5.3 Slug Fabrication

The cylinders formed in the sintering operation will be maintained in an inert atmosphere, compressed into a billet, and the metal extruded in the normal manner. The metal is not pyrophoric but will react with traces of oxygen present in the inert atmosphere. If necessary the cylinders will therefore be cleaned with acid before extrusion to remove any oxide film.

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*The specification is arrived at by comparison of the mercury slow neutron cross section with that of boron, whose permissible limit in thorium metal is 1 ppm.

$$\frac{(\sigma_{Hg})}{(\sigma_B)} \frac{(MW_B)}{(MW_{Hg})} = \frac{1}{39} \qquad 1 \text{ ppm B} \cong 39 \text{ ppm Hg}$$

An initial experiment on a single pellet showed that cold working was feasible, producing a plate without cracking with a Brinell hardness of < 60. After annealing, the hardness was Brinell 30. This is very soft thorium which should be excellent for extrusion purposes.

Both cold-pressed slugs and retorted cylinders have been subjected to melting at < 0.1 micron of pressure. The metal formed by this method was comparable to that obtained by retorting with the exception of the mercury content which was < 4 ppm.

Table 1

Analyses of Thorium Retorted at a Pressure of Less Than 0.1 Micron

Retorting Temperature (°C)	Total Heating Time (hr)	Density (g/cc)	Hg (ppm)	C (ppm)	O_2 (ppm)	N (ppm)	Na (ppm)	Brinell Hardness
800	0.5	---	650	---	---	---	---	---
900	0.5	7.55	400	330	6,500	190	---	---
1050	0.5	10.25	175	110	11,500	385	---	---
1000	0.5	7.68	210	210	16,400	160	---	---
1000	2.0	11.2	---	280	2,500	---	---	30*
1100	0.5	9.40	13	1,540	2,260	104	45	---
1100	1.0	9.57	20	530	1,750	560	---	---
1100	1.0	11.1	155	520	3,400	245	---	---
1100	2.0	9.05	45	156	2,750	200	---	---

*Cold rolled and annealed.

[redacted]

[redacted]

Figure 2 shows thorium metal from each Metallex processing step. Figures 3, 4, and 5 present photomicrographs of Metallex thorium. Figure 6 is a photomicrograph of typical Ames metal which has had treatment similar to that of the Metallex metal shown in Figure 4.

R. E. Blanco

R. E. Blanco

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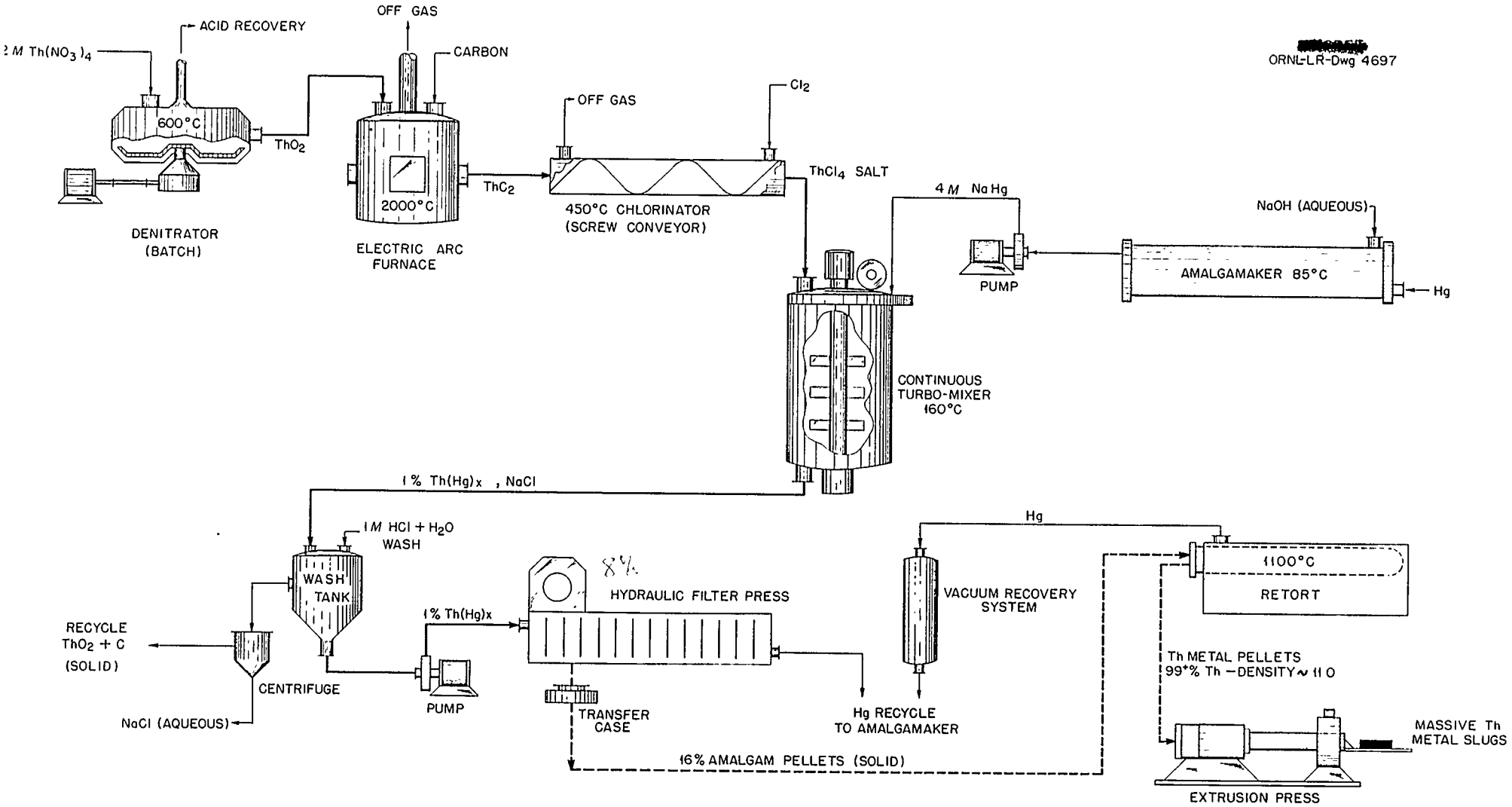

Fig. 1. METALLEX PROCESS

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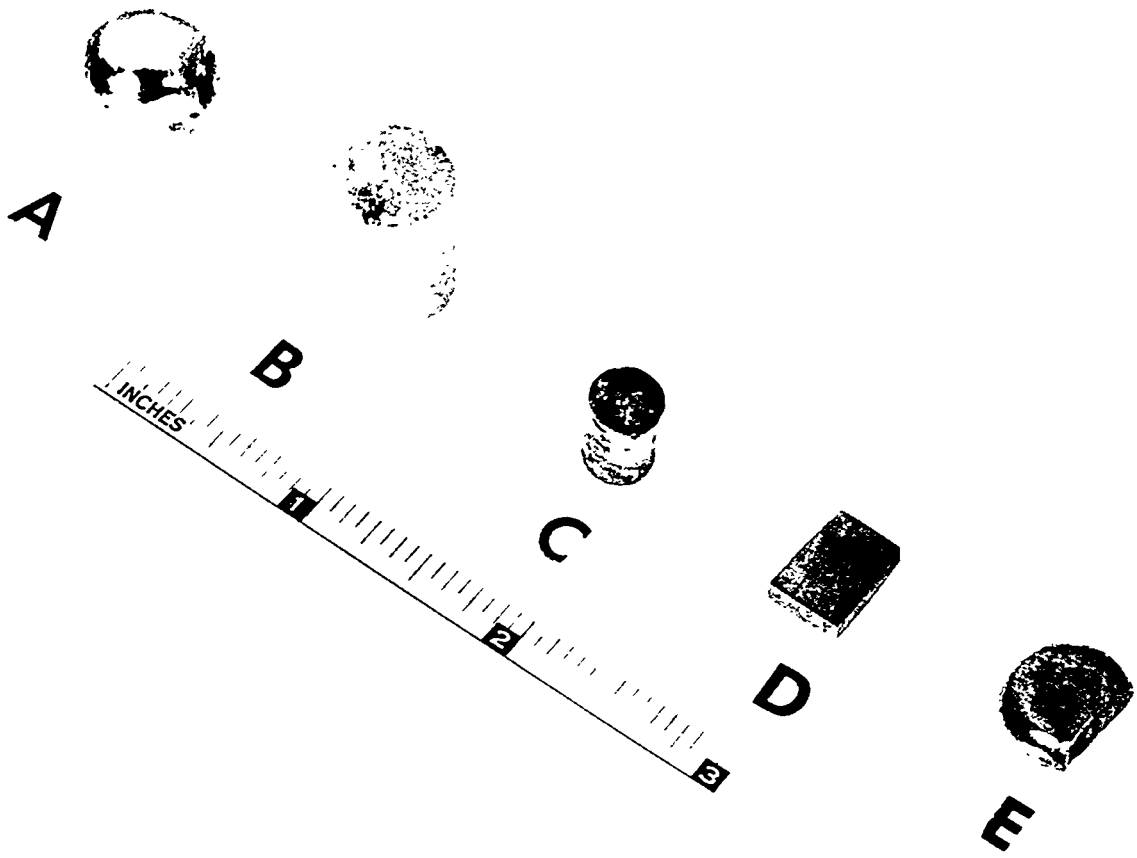

Fig. 2. Metallex Product From Various Processing Steps.

A- Amalgam filter cake-eight weight percent thorium.

B- Amalgam cylinder formed by cold die pressing - 16 weight percent thorium.

C- Thorium cylinder after retorting.

D- Sample C after cold working to 50% reduction in thickness.

E- Sample C after arc melting.

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Y-13832

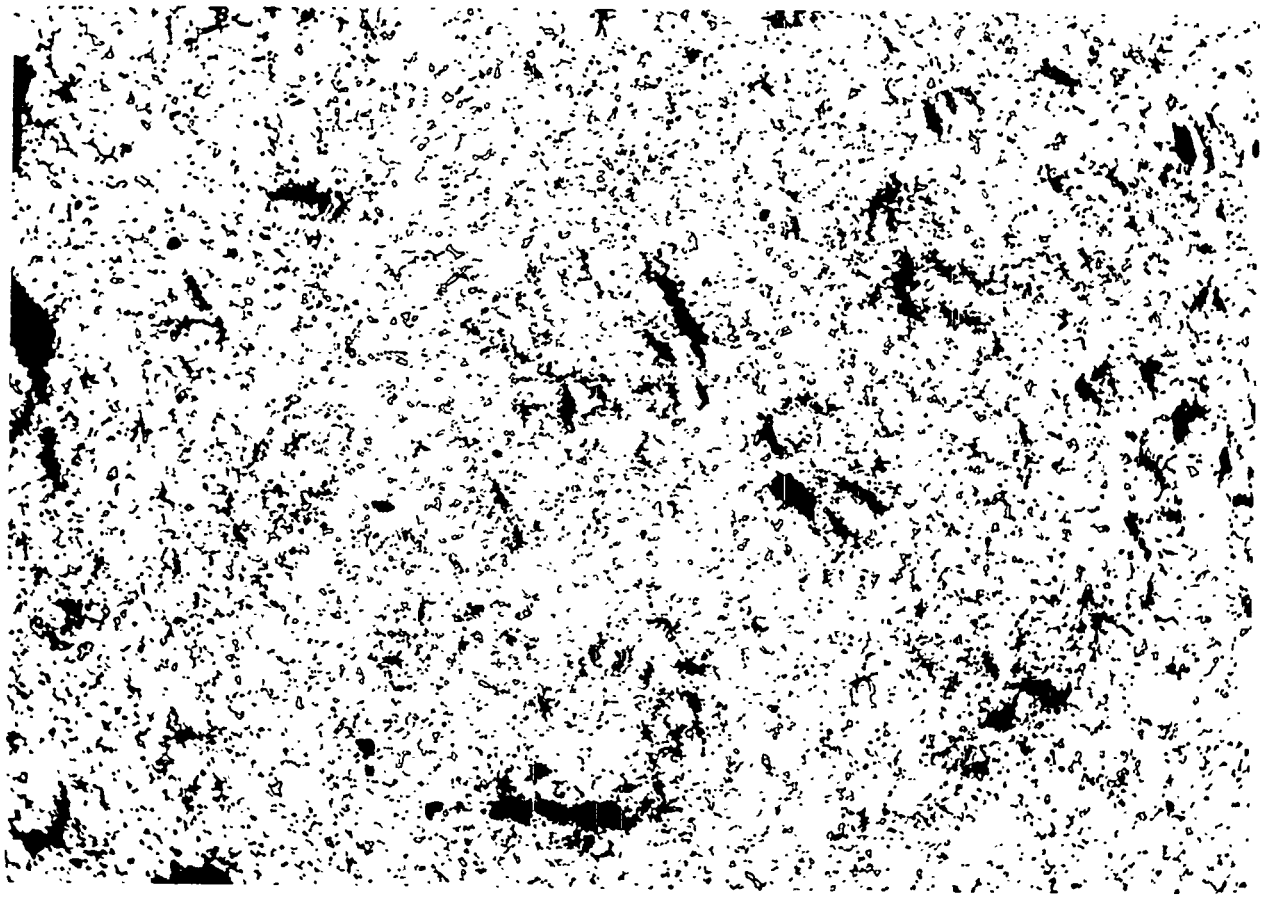

Fig. 3. Photomicrograph of Metallex Thorium Cylinder Retorted for 1/2 hour at 1000°C. 100X.

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Y-13938

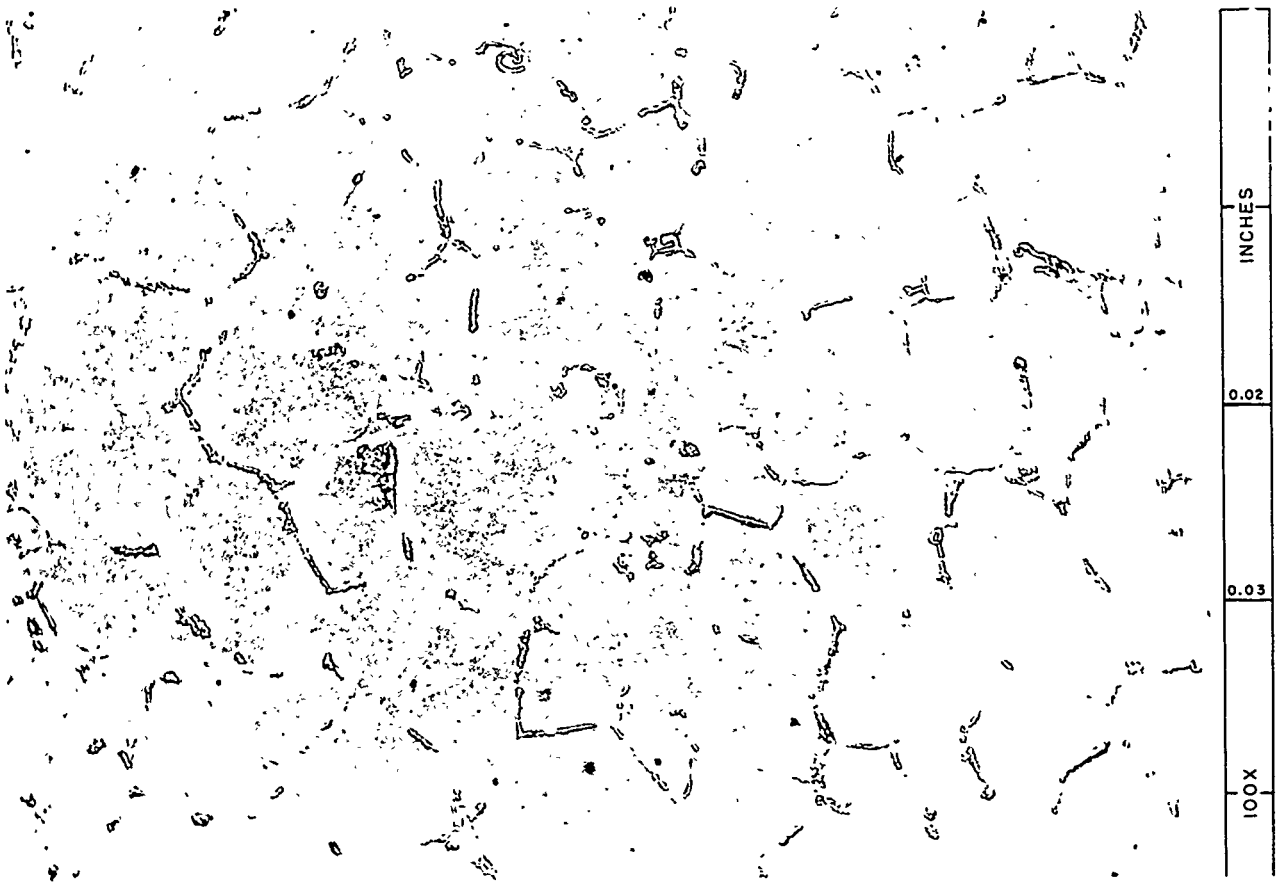

Fig. 4. Photomicrograph of Metallex Thorium Cylinder. 100X.

Retorted for 1-1/2 hours, cold worked to 50% reduction in thickness and vacuum annealed for 1-1/2 hours at 800°C.

The principal visible impurity is thorium carbide.

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Y-13874

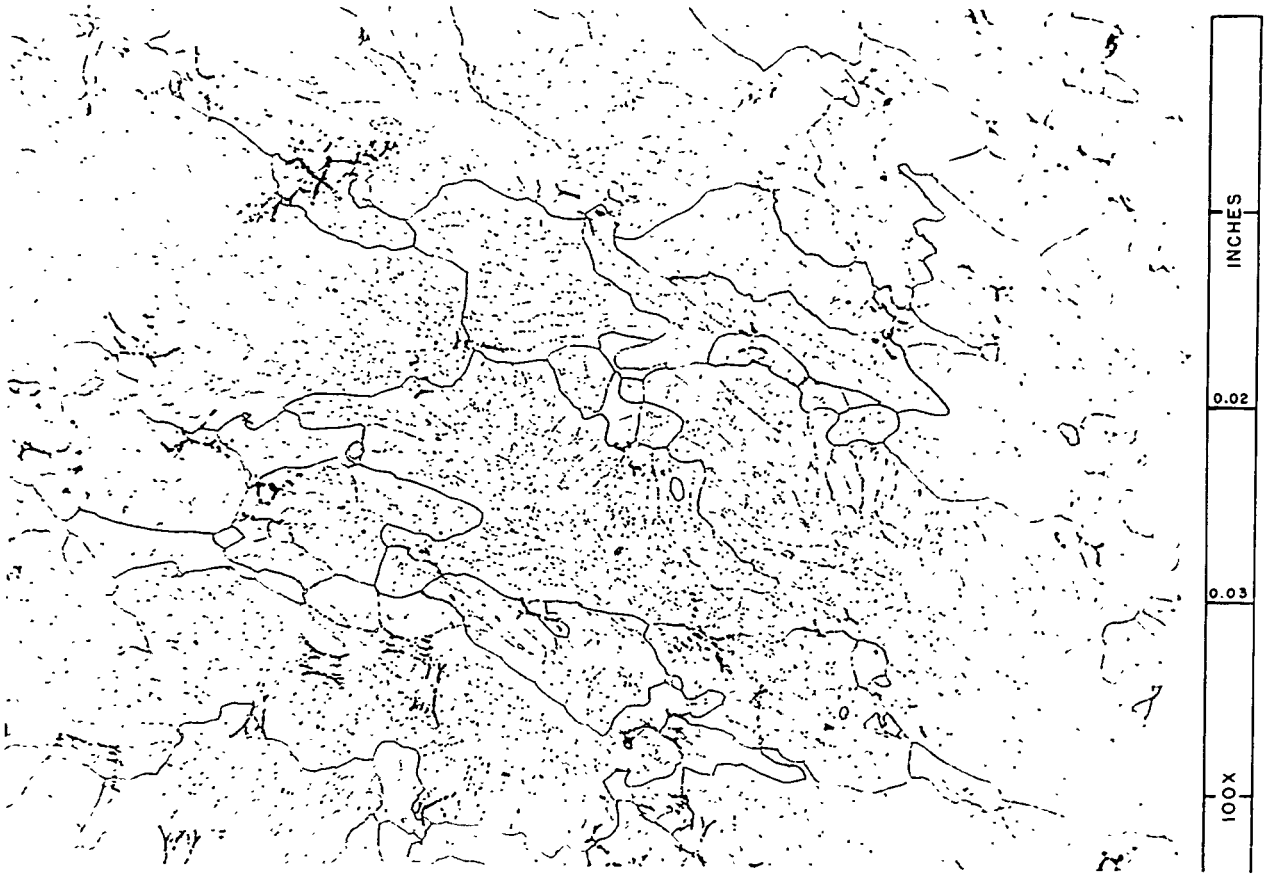

Fig. 5. Photomicrograph of Metallex Thorium Cylinder. 100X.

Retorted 1/2 hour at 1100°C followed by arc melting.

Y-14104

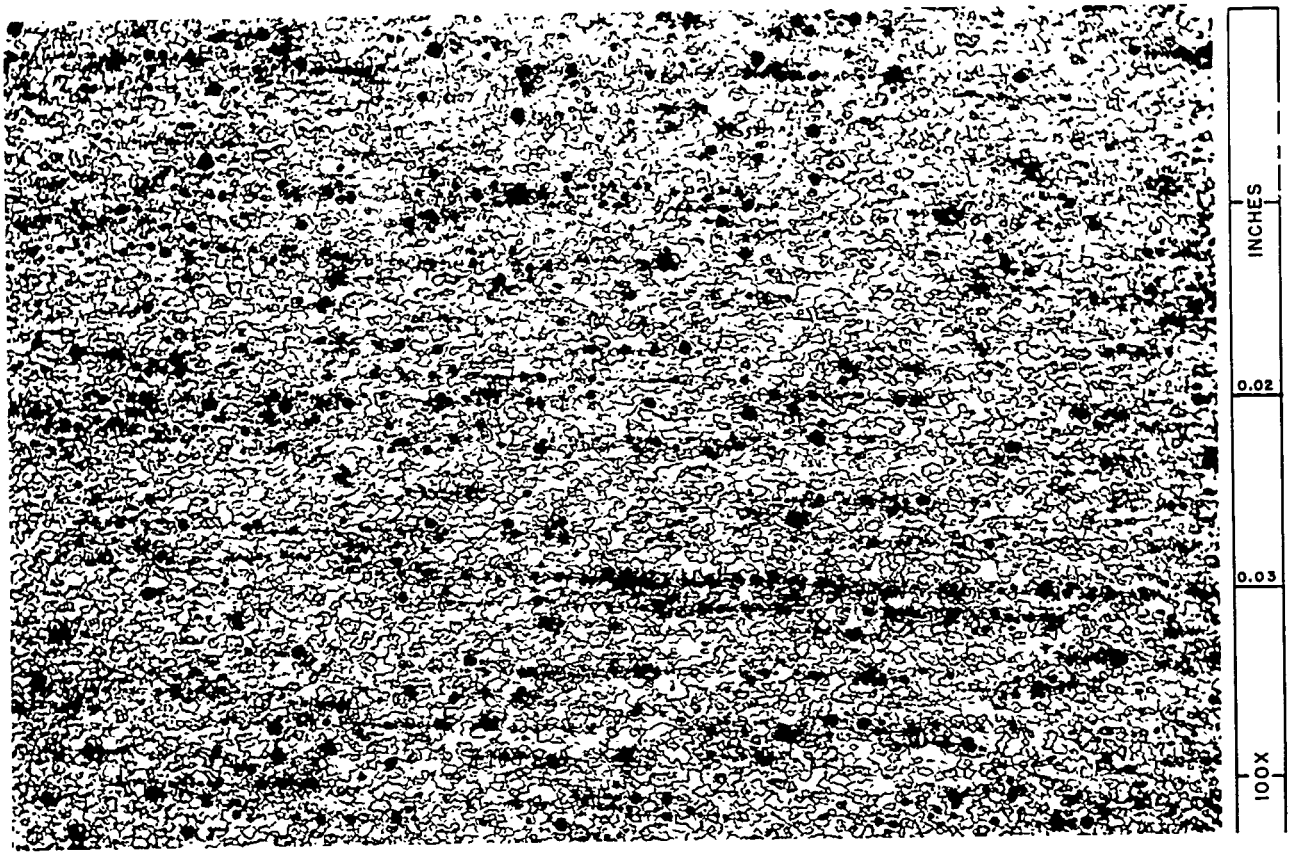

Fig. 6. Photomicrograph of Ames Thorium Metal. 100X.

Cold rolled to 85% reduction in thickness, annealed 1/2 hour at 742°C.

Principal impurity - Thorium oxide.

ROUGH DRAFT

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X-820

OAK RIDGE NATIONAL LABORATORY

Operated By

UNION CARBIDE NUCLEAR COMPANY

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL
CENTRAL FILES NUMBER
54-8-244

DATE: August 20, 1954

This document consists of 10 pages.
Copy 1 of 1 copies. Series CRD.

SUBJECT: Metallex Process - Flowsheet No. 2
Preliminary Cost Study

TO:

FROM: W. E. Schaeffer

Distribution

1. P. A. Mason, Ionics, Inc.

INV. 64

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ROUGH DRAFT

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

August 20, 1954

I.	PLANT INVESTMENT			
A.	Equipment Costs - delivered	$911,000		
B.	Equipment Costs - installed (1.43 x Item A)		$1,303,000	
C.	Processing Piping (45% of Item A, to which piping is connected)		346,000	
D.	Instruments - (10% of Item B)		130,000	
E.	Laboratory Equipment, Special		6,000	
F.	Process Buildings (20% of Item B, which is housed indoors)		257,000	
G.	Laboratory Building (1,200 sq ft at $75 per sq ft)		90,000	
H.	Service Facilities			
	New Site (25% of Item B)		326,000	
	Existing Site (5% of Item B)	65,000		
I.	Electrical Installations (15% of Item B)		196,000	
J.	Site Development (5% of Items A through I)		178,000	
K.	Total Physical Plant			$2,832,000
L.	Construction Overhead and Contractor's Fee (50% of Item K)		1,416,000	
M.	Engineering (20% of Item K)		566,000	
N.	Total of All Costs			4,814,000
O.	Construction Interest (2% of Item N)		96,000	
P.	Contingency (30% of Item N)		1,445,000	
Q.	Working Capital (Includes Material inventories, and "in process" materials, but no product storage, plus cash for one month's operation)		348,000	
R.	Preoperational charges (10% of annual operating cost less depreciation)		147,000	2,036,000
	TOTAL PLANT INVESTMENT			$6,850,000

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

August 20, 1954

	Cost	
ANNUAL OPERATING COSTS		
I. Variable Costs at 100% Capacity		
A. Operating Cost		
1. Raw material	$130,000	
2. Operating supervision	24,000	
3. Operating labor	130,000	
4. Control laboratory personnel and supervision	33,000	
5. Maintenance (12% of total physical plant)	340,000	
6. Operating supplies (0.6% of total physical plant)	17,000	
7. Utilities (estimate)	100,000	
8. Packaging and storage charges, spoilage and reruns, others (estimate at 5% of raw materials and direct labor)	26,000	
TOTAL ANNUAL VARIABLE COSTS		$860,000
II. Fixed Costs		
A. Investment Costs		
1. Depreciation (16% of total plant investment)*	1,096,000	
B. Penalty Charges and License Fees		
1. Penalty charge		
In holdup estimated at 6000 lbs assessed at 12% of value of raw material charge of $5.44/lb	3.86	
2. License fee or royalty		
Mathieson Chemical Company assessed on basis of 6.67 year plant life $0.18 2/3 per cell ampere	2.17	
TOTAL ANNUAL CHARGES	6,000	
C. Overhead (estimated at 100% of direct labor and supervision plus maintenance plus supplies)	604,000	
TOTAL ANNUAL FIXED COSTS		$1,706,000
TOTAL ANNUAL OPERATING COSTS		$2,566,000
Cost, Dollars per Pound	$1.28	

*Land cost not known and neglected.

[redacted]

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

August 20, 1954

EQUIPMENT COSTS, DELIVERED

a.	Amalgamator section, incl. eng.	$174,300
b.	Solvent drying section, incl. eng.	14,400
c.	Induction furnaces, incl. eng.*	374,114
d.	Other major equipment	300,800
e.	Vessels, excluding any included in a and b	23,545
f.	Condensers, excluding any included in a and b	2,000
g.	Agitators, excluding any included in a and b	7,600
h.	Pumps, excluding any included in a and b	12,053
i.	Inert gas drying system	2,500
	TOTAL DELIVERED EQUIPMENT COSTS	$911,312

*Cost assumes 2 banks of 2 furnaces each with common vacuum and high frequency equipment.

[redacted]

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

August 20, 1954

	Manhours/ 24 hr. day	Annual Cost
DIRECT PROCESS LABOR		
A. Operating Labor		
1. Solvent drying	16	
2. Feed preparation	24	
3. Amalgamaker section	48	
4. Mixer settlers	--	
5. Separation and drying	24	
6. Furnace operation	48	
7. Recovery operation	48	
Total Manhours	208	$130,000
B. Direct Supervision		
(Assume 3 men at $8,000 per year)		24,000
TOTAL OPERATING LABOR* AND SUPERVISION		$154,000

*Estimated at $2.50/hr, excluding overhead.

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

August 20, 1954

	Average Annual Salary	Annual Cost
LABORATORY PERSONNEL, TOTAL FOR THREE SHIFTS		
a. Chief chemist	$7,000	$ 7,000
b. Chemists and shift supervisors, 3	6,000	18,000
c. Technicians, 15	4,500	67,500
TOTAL		$92,500

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

August 20, 1954

[redacted]

	Pounds	Unit Value	Total
WORKING CAPITAL			
1. Material Inventory*			
EDA	10,770	$ 1.00	$ 10,770
Mercury	79,100	2.60	205,700
Th, raw material cost excluded	6,000		
Diphenyl	560	.47	263
Benzene	3,670	.048	176
NaOH	54,500	.061	3,324
HNO_3	400	.06	24
Helium** 56 cylinders		39.20	2,195
Nitrogen** 100 cylinders		34.50	3,400
			$225,900
2. Cash for one month's operation (estimated as 1/12 annual variable operating costs plus overhead)			$122,000
TOTAL WORKING CAPITAL			$347,900

*Includes raw material storage and 'in process' materials, but no product storage.

**Assumes $34.00 deposit/cylinder.

[redacted]

[redacted]

[redacted]

METALLEX PROCESS - FLOWSHEET NO. 2

Preliminary Cost Study

[redacted]

August 20, 1954

	Lbs/Hr	Unit Values	Daily Totals	Annual Totals
RAW MATERIALS				
1. Raw Materials Consumed*				
$ThCl_4$, as Th	366	$5.44	Excluded	
Sodium Hydroxide, flake, drum	227	.061	$332.40	$83,100
Nitric Acid	1.66	.06	2.39	600
Helium 3 cyl/day		5.20	41.60	10,400
Nitrogen 20 cyl/day		.50	10.00	2,500
Subtotal			$386.48	$96,600
2. Inventory Losses				
Th	3.76	$5.44	24 hr/d Excluded	5d/wk, 50 wk/yr
Hg	1.93	2.60	$120.43	$30,100
PDA	.60	1.00	14.40	3,600
Subtotal			$134.88	$33,700
TOTAL RAW MATERIAL COST			$521.36	$130,300

11,600 lb. Hg

*Based on local costs, additional reductions possible on tank shipments.

[redacted]

[redacted]

HORIZONS, INC., PROCESS COST ESTIMATE ON COMPARABLE BASIS TO METALLEX COST ESTIMATE OF AUGUST 20, 1954

		Cost	
I.	PLANT INVESTMENT		
A.	Direct materials - less roadways and sewers	$4,234,000	
B.	Direct labor - less roadways and sewers	2,124,000	
C.	Total	$6,358,000*	
D.	Site development (5% of Items A and B)	318,000	
E.	Total physical plant	$6,676,000	
F.	Construction overhead and contractor's fee (50% of Item E)	3,338,000	
G.	Engineering (20% of Item E)	1,336,000	
H.	Total of all costs		$11,345,000
I.	Construction interest (2% of Item H)		227,000
J.	Contingency (30% of Item H)		3,405,000
K.	Working capital (assumed 1/25 total raw material cost plus cash for one month's operation)		154,000
L.	Preoperational charges (10% of annual operating cost less depreciation)		318,000
	TOTAL PLANT INVESTMENT		$15,454,000

*Purely coincidental to figure given for Grand Total Cost, Turnkey Basis given in Horizons', Inc., Cost Report.

HORIZONS, INC., PROCESS COST ESTIMATE ON COMPARABLE BASIS TO METALLEX COST ESTIMATE OF AUGUST 20, 1954

		Cost
ANNUAL OPERATING COSTS		
I. Variable Costs at 100% Capacity		
A. Operating Cost		
1. Raw material	$156,000	
2. Operating supervision)		
3. Operating labor)	457,000	
4. Control laboratory personnel and supervision	93,000	
5. Maintenance (12% of total physical plant)	301,000	
6. Operating supplies (0.6% of total physical plant)	40,000	
7. Utilities (estimate)	195,000	
8. Packaging and storage charges, spoilage and reruns, others (estimated at 5% of raw materials and direct labor)	31,000	
TOTAL ANNUAL VARIABLE COSTS		$1,773,000
II. Fixed Costs		
A. Investment Costs		
1. Depreciation (16% of total plant investment)*	2,473,000	
B. Penalty Charges and License Fees		
1. Penalty charge Th holdup estimated at 6000 lbs assessed at 12% of value of raw material charge of $5.44/lb	3.86	
License fee or royalty - Mathieson Chemical Company assessed on basis of 6.67 year plant life $0.18 2/3 per cell ampere	2.17	
Total Annual Charges	11,000	

[redacted]

Overhead (Estimated at 100% of direct labor and supervision plus maintenance plus supplies)	$1,391,000	
TOTAL ANNUAL FIXED COSTS		$3,875,000
TOTAL ANNUAL OPERATING COST		$5,648,000
Cost, Dollars per Pound		$2.824

*Land cost not known and neglected.

[redacted]

X-831

OAK RIDGE NATIONAL LABORATORY
Operated By
UNION CARBIDE NUCLEAR COMPANY
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

DATE: February 4, 1957

SUBJECT: Metallex Objectives

TO: F. L. Culler

FROM: O. C. Dean

DISTRIBUTION

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18. W. E. Unger
19. C. E. Winters
20-21. Laboratory Records
22. Laboratory Records-RC
23-24. Central Research Library

There are four immediate objectives in the laboratory Metallex program:

Objective 1

To determine the feasibility of taking the reduction product ($ThHg_3$) into solution in mercury by refluxing at the boiling point of mercury after completing the reaction at 130-150°C.

Justification: At the end of the reaction at 130°C the quasi product, oxides, NaCl, and unreduced $ThCl_4$ float on the mercury, and byproducts can be separated from product only by aqueous washing. Aqueous washing is suspect for a source of above-specification oxygen and hydrogen in the sintered metal, due to residual water in the amalgam going to the retorting step. Also, water is thought to be the reason for porosity of sintered metal. Solution of $ThHg_3$ in mercury, hot filtration, and recrystallization offer a possibility for eliminating aqueous washing as a separation step. Three experiments using glass apparatus and sintered glass filters failed to show a passage of more than 50% of the reduced thorium through the filter. However, all of the byproducts were removed. There were strong indications that the hot thorium amalgam reacted with the sintered glass, forming and plugging the filter with ThO_2. Also it was suspected that the filter temperature was below the boiling point of mercury.

One experiment, conducted in stainless steel in which the reaction was carried out at 356°C, and the product filtered through a hot sintered stainless filter, showed that 60% of the reduced thorium passed through the filter. It was impossible to keep the filter at 356°C without injury to the packing of the valve below it. It was thought that results were not completely satisfactory only because of physical equipment difficulties.

An alternate approach to hot filtration in the same scheme is to reflux the product at 356°C, then allow to settle, slagging off the

oxide, NaCl, etc., and collecting the more concentrated $ThHg_3$ at the bottom. It has been shown that the $ThHg_3$ has higher density than Hg, and should separate by centrifugation or settling.

To overcome the disadvantage of the higher oxygen-reactivity of the amalgam formed at higher temperatures, it is proposed that the thickened product from the bottom be introduced to the top of a vertical sintering furnace without pelletization or other handling (see objective 2 and Fig. 1). The possibility of carrying out the whole operation without contact with oxygen-bearing material is attractive.

Objective 2

To produce sintered metal from 3% quasi by progressive mercury removal without pelletization, and to make the process continuous.

Justification: Earlier experiments carried out by Metallurgy showed that sintered metal could be made in a boat without pressing from about 5% quasi. The sintered metal took the form of the boat. In view of the findings by Armour, it is thought that a scheme as pictured in Figure 1 would produce a sound billet continuously.

Such a scheme might also be applied to Hermex with the U-melting modification.

The success of objective 2 would lead to the Metallex flowsheet in Figure 2.

Objective 3

To test the feasibility of a scheme by which impure metal may be electrolytically dissolved in a low-melting fused salt and redeposited in a mercury pool cathode, then reprocessed by the Hermex or Metallex furnace to pure metal. This is a longer range objective.

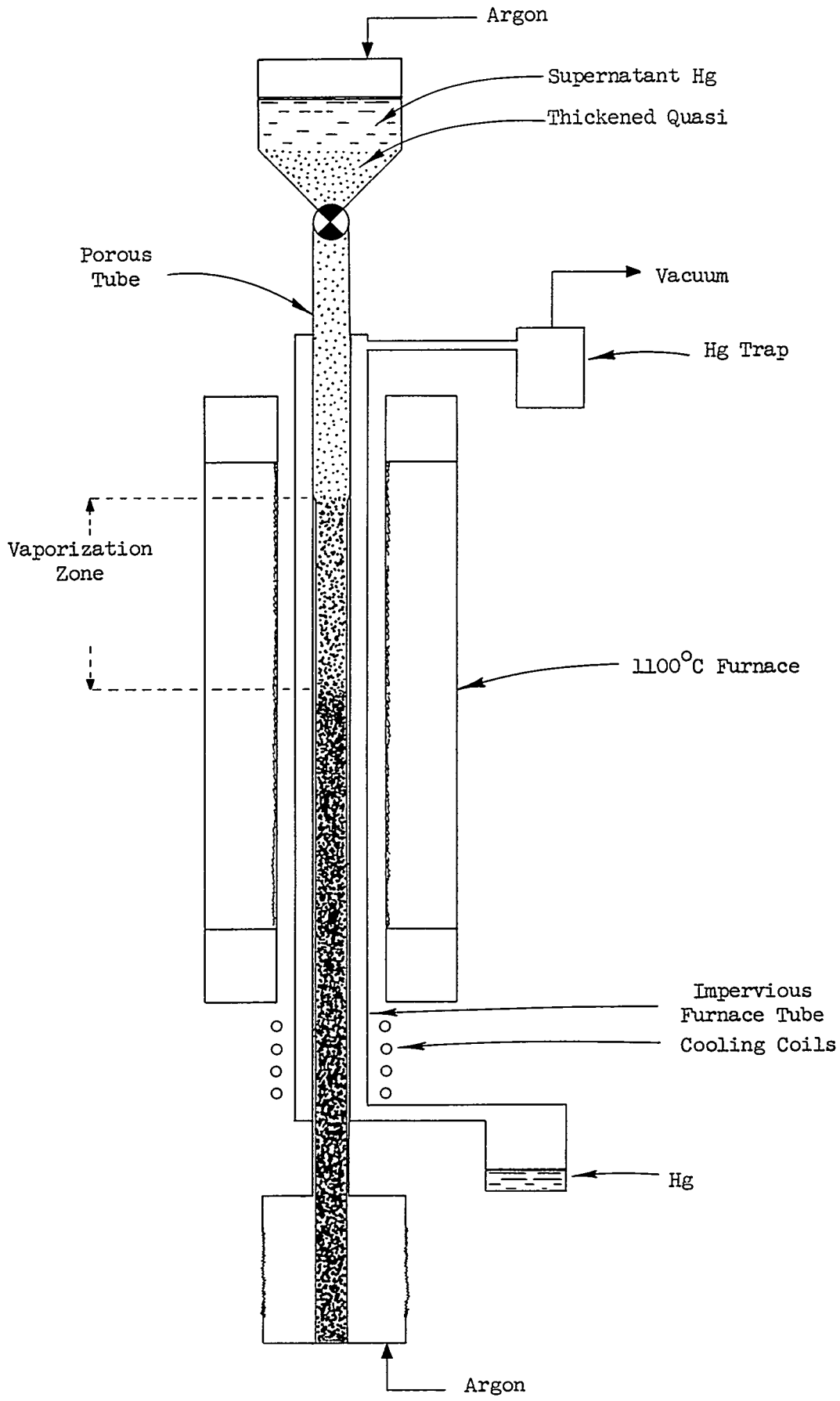

Fig. 1 VERTICAL AMALGAM RETORT

ORNL-LR-Dwg #18667

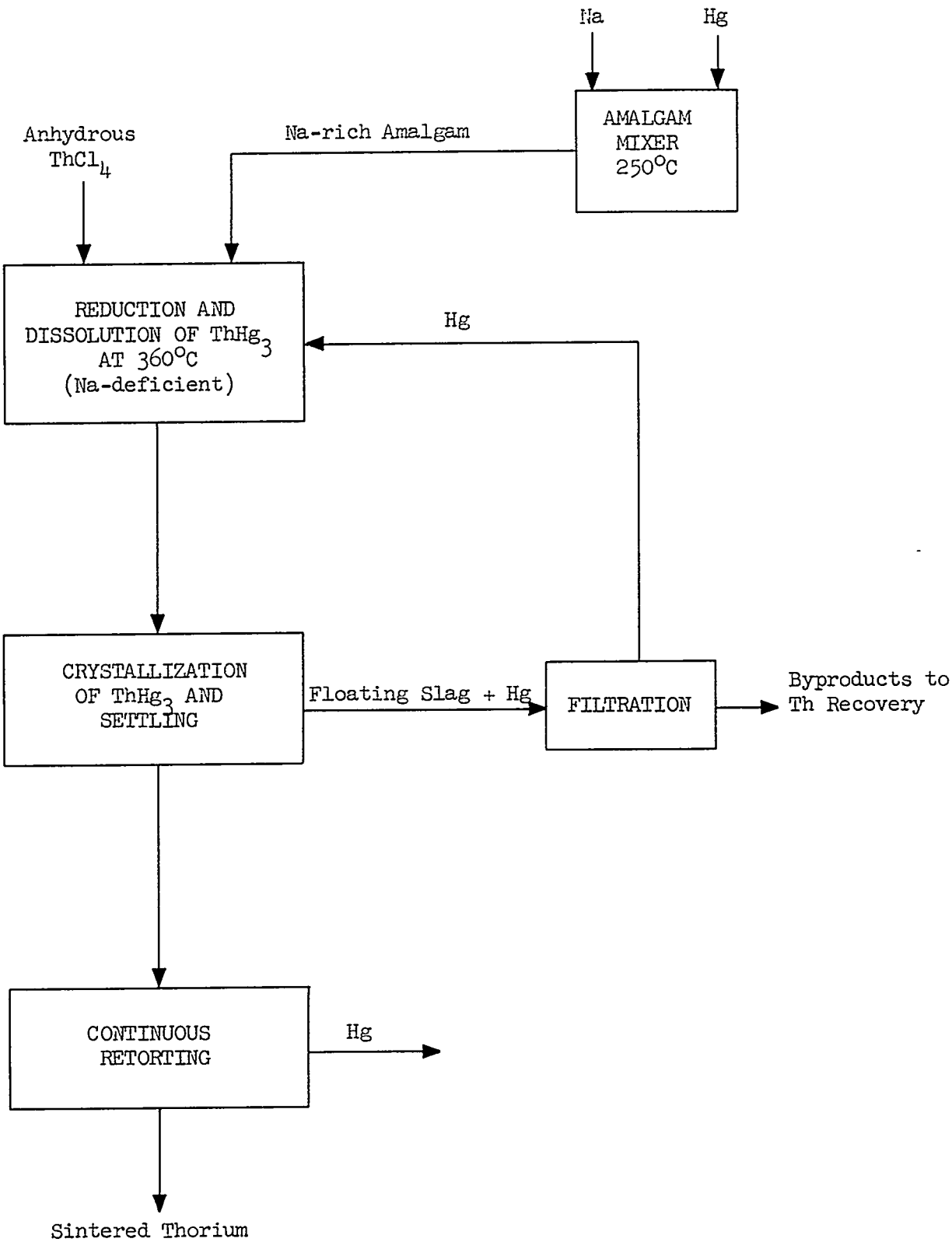

Fig. 2 SCHEMATIC FLOWSHEET FOR METALLEX NON-AQUEOUS MODIFICATION

Objective 4

To further study the reaction $UF_6 + 6NaHg_x \longrightarrow UHg_4 + Hg + 6NaF$ at 360°C, with separation of the reaction byproducts by filtration at 360°C. The UHg_4 is to be recovered from the mercury by the established Hermex route. The sodium concentration in the amalgam will be varied at this temperature. A variation will be to carry out the reaction cold, (< 100°C) digest and reflux at 360°C, then hot-filter.

O. C. Dean

O. C. Dean

OCD/jr

2788

AEC RESEARCH AND DEVELOPMENT REPORT

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DATE: April 11, 1955

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For Period of March 21, 1955 to April 1, 1955

TO: ~~W. A. Jenkins~~

FROM: F. L. Culler

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UCC

POST OFFICE BOX P
OAK RIDGE. TENN.

April 11, 1955

Mr. W. A. Jenkins
E. I. duPont de Nemours Company
Explosives Department
Wilmington 98, Delaware

Dear Bill:

25. Use of Thorex-type high temperature feed digestion at high HNO_3 concentrations will prevent subsequent organic emulsion formation in the 25 extraction column, even when the dissolver solution is known to contain emulsion-producing impurities. Gross D.F.'s for three spiked-feed small pulse column runs were at least 3×10^4 β and 5×10^3 γ across both columns. Trickle dissolver tests using 2S Al sheet in the 5-in. D pipe unit yielded a 5 ft. packed height for a processing rate of 200 kg Al/day, equivalent to ~ 20 kg U/day when dissolving SR tubular elements. The packed height dropped to just under 3 ft. when the dissolving rate was cut in half.

Metallex. Thorium metal quality studies indicate that metal samples prepared by arc-melting sintered compacts are within target specifications (as set forth in DPST 54-582, Nov. 1954) except for the iron content. The Abbie "Dispersall" mixer has been tested briefly for the dry-$ThCl_4$ contacting with NaHg and probably will prove satisfactory for making 0.5 lb. batches of Th as quasi amalgam.

Very truly yours,

F. L. Culler

F. L. Culler, Director
Chemical Technology Division

FLC:ACJ/pms

Attachment (1)

1.0 25 PROCESS ASSISTANCE

1.1 1A Column Chemistry

Work is continuing on the organic emulsion problem under 1A column feed-plate conditions. Application of variations of the Thorex head-end treatment, i.e., dehydration of feed impurities by high temperature digestion at high nitrate concentrations, has been studied using an emulsion-producing 2S Al bar-stock dissolver solution (1.8 M Al, 1 M H^+, 0.008 M Hg^{+2}) as the 1AF. These experiments are summarized in Table 1. The results indicate that 3 hours digestion at the boiling point in the presence of 8 M HNO_3 at Al concentrations of 2 to 4 M, prior to readjustment to 1AF flowsheet conditions, will prevent organic emulsion formation. The treated 1AF's (unfiltered) were batch-equilibrated for 1-1/2 minutes with 6% TBP-Amsco in the presence of neutral 0.75 M $Al(NO_3)_3$ - 0.02 M $Fe(NH_2SO_3)_2$ scrub, using the volume ratio AF:AS:AX = 100:20:40, and the presence or absence of stable emulsions noted. Apparently the presence of H^+ ion during digestion is necessary for the dehydration, since digestion of ~5 M Al with essentially no acid present (see Experiment No. 3, Table 1) did not eliminate emulsion formation. In all other runs, a clear aqueous phase was obtained in 20 to 30 seconds and the organic cleared in 65-80 seconds, leaving a clean interface.

An attempt was made to produce emulsion by adding trace impurities to synthetic feed. This feed was batch equilibrated with 6% TBP-Amsco in the presence of 0.75 M $Al(NO_3)_3$ - 0.02 M Fe $(NH_2SO_3)_2$ - 3.0 M HNO_3 scrub solution with the feed:scrub:solvent volume ratio of 100:20:40. Trace impurities (Fe, Mn, Cu, Ni, Ag, V, Ca, Mg, Si) in the same concentrations as determined by spectrographic analysis of 2S Al bar-stock were "spiked" into the system one at a time and the phase disengagement times noted after such addition. Although some variation of disengagement time was seen, no stable emulsions were produced by this method. Therefore, it was concluded that the impurities known to be present in the bar-stock must exist in different forms in actual dissolver solution.

1.2 0.75" Diameter Pulsed Column Facility

1.21 Batch Dissolution of Dummy SR Fuel Elements

SR dummy fuel element #D-99 (2350 grams total weight) was dissolved in 50 liters of 7.4 M HNO_3 containing 0.005 M $Hg(NO_3)_2$. The reaction was initiated by heating to 90°C, and then controlled by applying cooling water for about 1 hour. Steam was then reapplied to maintain the dissolver at ~105°C. Table 2 shows the results of periodic sampling, and indicates that the element was essentially completely consumed within a period of about 2 hours or less.

Table 1

Feed-Al bar-stock dissolver solution:

1.8 M Al
1.0 M HNO_3
0.008 M H^{+2}

Standard equilibration test for emulsion:

50 ml of designated 1AF
10 ml neutral 0.75 M $Al(NO_3)_3$ - 0.02 M $Fe(NH_2SO_3)_2$ as 1AS
20 ml of 6% TBP-Amsco as 1AX
Equilibrate 1-1/2 minutes

Experiments No.	Dissolver Solution Pretreatment	Observations
1	Evaporate to 1/4 vol.; add equal vol. 16 M HNO_3; digest 3 hr. Evaporate off acid (142°C) and readjust to 1.0 M H^+ and 1.8 M Al.	No stable emulsion
2	Evaporate to 1/2 vol. (130°C) add equal vol. 16 M HNO_3; digest 3 hr. Evaporate off acid (130°C); add equal vol. of 2 M HNO_3: H^+ = 2.3 N, Al = 1.8 M.	No stable emulsion
3	Evaporate to 1/3 vol. (135°C), digest 3 hr. Add back condensate: H = 1.0 M, Al = 1.8 M.	Obtained stable emulsion
4	Evaporate to 1/2 vol. (130°C); add equal vol. 16 M HNO_3; digest 3 hr. Evaporate off acid (130°C); dilute back to original volume with H_2O: H = 1.0 M, Al = 1.8 M.	No stable emulsion

(Note: In all cases a clear aqueous phase was obtained in 20 to 30 sec.; with the exception of Experiment No. 3, a clear organic phase was obtained in 65-80 seconds.)

Table 2

Dissolution of Dummy ~~SR Tubular~~ Fuel Element in 7.4 M HNO_3-0.005 M $Hg(NO_3)_2$

Dissolving Time Hours	H^+ Conc., M	~~U~~ Conc., mg/ml	Al Conc., mg/ml	Volume, liters	Weight Dissolved
0.5	1.76	2.89	36.7	50	84.5
1.0	--	3.80	40.9	--	--
2.0	0.74	4.12	42.7	--	--
2.5	--	3.97	43.7	--	--
3.0	0.79	4.01	44.1	--	--
3.5	--	4.05	47.2	--	--
4.0	0.83	4.01	44.3	48	99

1.22 Flowsheet Testing

To date, three column runs were made utilizing feed prepared by dissolving dummy ~~SR tubular~~ fuel elements, digesting, filtering, and spiking with fission products from irradiated U-Al alloy. Runs HCU-1 and HCU-2 were of 7 hours duration and Run HCU-3 lasted 11 hours. The following flowsheet conditions were used:

1AF/75 ml/min = 3.8 g U/l, 1.0 M HNO_3, 1.8 M $Al(NO_3)_3$, 0.005 M $Hg(NO_3)_2$, 1.5 - 5.0 x 10^7 Gross β c/m/ml, 3.4 - 8.1 x 10^7 Gross γ c/m/ml.

1AX/30 ml/min = 6% TBP in Amsco Special Naptha No. 1

1AS/15 ml/min = 0.75 M $Al(NO_3)_3$, 3.0 M HNO_3, 0.02 M $Fe(NH_2SO_3)_2$

1BX/11 ml/min = 0.01 M HNO_3

Results of run HCU-1 (AF = 1.5 x 10^7 Gr β c/m/ml) indicated that the A column had reached equilibrium with respect to the fission products at the end of about 5 hours (~6.5 volume changes), and that the B column had reached equilibrium at the end of about 6 hours. The Gross β decontamination factor (D.F.) across the A column was about 2 x 10^4, and about 8 x 10^4 across both columns; the Gross γ DF across both columns was 1 x 10^4.

Table 3 shows decontamination data from Run number HCU-2 (AF = 2.5 x 10^7 Gr β c/m/ml).

Table 3

First Cycle Decontamination - Run No. HCU-2

F.P. Activity	1AF, c/m/ml	1BP, c/m/ml	DF
Gross β	2.47 x 10^7	4.08 x 10^3	2.57 x 10^4
Gross γ	9.42 x 10^6	7.40 x 10^3	5.33 x 10^3
Ru β	1.38 x 10^6	148	3.91 x 10^4
Zr γ	1.81 x 10^6	2.3 x 10^3	3.29 x 10^3
Nb γ	3.62 x 10^6	2.4 x 10^3	6.32 x 10^3
TRE β	1.53 x 10^7	< 10^2	> 10^5

Results of Run HCU-3 confirmed these decontamination factors on a feed having about twice the gross activity of that in HCU-2. The decontamination factors for Gross β and Gross γ activities were 3 x 10^4 and 5 x 10^3, respectively. Results of individual fission product decontamination are not presently available.

Column operation was very smooth throughout all runs, and essentially no interfacial material or emulsions built-up during the operation.

1.3 Mixer-Settler Facility

An excessive amount of difficulty with the Zenith metering pumps, caused by corrosion of internal parts (made of Type 400 stainless steel) in contact with TBP in Amsco, necessitated frequent shutdowns and repairs. All solutions in contact with the pumps have been changed to either water or straight Amsco in an effort to keep the pumps operating.

Pump failures ruined the tracer level run that had been started in the mixer-settler unit. Another run is scheduled for 3-28-55.

1.4 Trickle Dissolver Tests

Two trickle dissolvings of 2S Al sheet have been made in the 5-in. D pipe system. A packed height of 5 ft. was obtained in one run made at a processing rate of 200 kg Al/day (equivalent to ~20 kg U/day in SR tubular elements), while in a run at one half this rate the packed height was just under 3 ft. The results of these two runs parallel the results obtained earlier for Al slugs, but the rate vs. packed height curve is shifted to roughly a 65 kg/day higher rate for all packed heights.

About 10 g solids (mostly magnetic) was found in the bottom of the dissolver following the dissolution of about 500 lbs. of 2S Al. These solids dissolve in HNO_3. Analyses are currently being performed.

2.0 METALLEX

2.1 Reduction of $ThCl_4$ with NaHg

Experiments were continued in which $ThCl_4$ powder was reacted with NaHg in glass apparatus at temperatures ranging from ~130-230°C using pitched blade agitators and no baffling in the system. Analytical results of these experiments show ~80-90% reduction of $ThCl_4$ to Th quasi amalgam based on analysis of acid and water wash solutions, in experiments carried out about 160°C. In one experiment a maximum temperature of 153°C was recorded and a low conversion of $ThCl_4$ to thorium amalgam of ~25% was found.

Other experiments were carried out by W. Schaffer in which a small Abbie "Dispersall" mixing unit was used as a reactor. This unit may be described as containing a mixing device somewhat similar to a coffee mill. It provides a high shear to the reactants and may be operated at variable speeds. Analysis of reactants from the initial run using this equipment while operating at a temperature range of ~25-145°, and containing 195 gm Th as $ThCl_4$ produced a good grade of quasi amalgam with a yield of >50% $ThCl_4$ reduction to Th amalgam. Incomplete analysis of later runs show this apparatus to be well suited to production of thorium quasi amalgam on a scale of the order of ~1/2 to 1 lb. Th per run.

Reduction of ThO_2 by NaHg

Experiments were carried out in an attempt to react ThO_2 (produced by thermal decomposition of $Th_2(C_2O_4)_2$ at 650°C) with NaHg, without success. The reactants mixed extremely well, and visually appeared as the reactants did when $ThCl_4$ is used in place of ThO_2. However, on washing the amalgam or dry filtering to separate the bulk of the Hg, no quasi or Hg containing Th was found. Likewise, the usual black thorium-mercury compound was not observed. Runs with ThO_2 prepared at lower temperatures, as well as dried $Th_2(C_2O_4)$ and $ThOCl_2$, are planned.

2.2 Metal Quality Studies

Samples of metal prepared by arc-melting sintered compacts showed the following properties:

Table 4

Component	Sample 1	Sample 2	Sample 3
ThO_2, by HCl-insoluble	0.58%	0.76%	0.59%
HNO_3-HF insoluble	0.45%	0.40%	0.35%
Oxygen by vacuum fusion	480 ppm	1220 ppm	420 ppm
Nitrogen by vacuum fusion	225 ppm	330 ppm	190 ppm
Nitrogen by Kjeldahl	150 ppm	330 ppm	190 ppm
Carbon	400 ppm	440 ppm	430 ppm
Hydrogen by vacuum fusion	8.2 ppm	13.0 ppm	7.8 ppm
Iron	1200 ppm	650 ppm	1100 ppm
Mercury	21 ppm	17 ppm	9 ppm
Sodium	12 ppm	<10 ppm	<10 ppm
Annealed density	11.67	11.65	11.63
Hardness as cast, R_B	10, 10, 12	34, 34, 32	7, 11, 13
Hardness as annealed, R_B	<0, <0, <0	24, 25, 26	3, 6, 2

All properties except iron content are within target specifications as set up by the Quality Working Committee on Thorium Specifications (DPST 54-582) Nov. 1954. It is of interest to note that chemically, the only significant differences which might account for the higher hardness of sample no. 2 are oxygen and hydrogen.

A study of possible reasons for spalling and cracking of sintered compacts showed that impurity contents of ThO_2 below 3.0%, sodium below 100 ppm, carbon, nitrogen, hydrogen and mercury in the quantities encountered prior to arc melting could not account for this type of behavior. Sodium ranged between 30 and 240 ppm; ThO_2 between 1.0 and 3.9%; Hg between 4 and 730 ppm; carbon between 210 and 790 ppm; nitrogen 72-310 ppm; hydrogen, 4 to 80 ppm. Sodium content above 100 ppm and ThO_2 above 3.0% appeared to increase cracking of sinters.

2.3 Phase Study of the Thorium-Mercury System

Studies of the thorium amalgams indicate that the $ThHg_3$ hexagonal close packed phase is stable at elevated temperatures (about 200°C) in the presence of free mercury. At room temperatures in the presence of free mercury a new phase appears which is identified by its X-ray diffraction pattern. This new phase (phase II) exhibits intense diffractions of the Cu K α X-rays at Bragg angles of 14.0°, 17.5° and 29.0°. This phase II forms slowly and becomes observable when the amalgam has been at room temperature for several days. Also phase II is the only solid phase found in amalgams which had been formed by low temperature reductions, 50°C.

Studies of the amalgam from the pressing step following filtration of the amalgam indicate that as the thorium concentration increases from 4 to 15% the amount of the $ThHg_3$ hexagonal close packed phase increase and the amount of the phase II decreases.

X-831

[redacted] COVER SHEET ORNL MASTER

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57-5-47

DATE: May 8, 1957

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FROM: C. D. Scott

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[redacted] COVER SHEET

Problem Leader: C. D. Scott

Problem Schedule: April 1957 through June 1958

1.0 Origin of Problem

Since much of the UF_6 product and tails from the Gaseous Diffusion Process is reduced to metallic uranium, there is need for a process to perform this reduction. The present process for this reduction involves two major steps: (1) continuous hydrogen reduction of UF_6 to UF_4 and (2) batch reduction of UF_4 to metallic uranium by calcium or magnesium.

If the direct and continuous reduction of UF_6 to metallic uranium is possible, a savings could be realized both because of the elimination of one major process and because of the elimination of all major batch operations. It has been established that if the Y-12 Plant alone could replace their present process with a continuous, direct reduction of the type being considered here, they would realize a savings of approximately $200,000/month.(1)

Several different workers have reported limited amounts of work on the direct reduction of UF_6 to metallic uranium.(2)(5)(7) Some of the data which are available indicate that metals such as calcium, magnesium, and sodium will reduce UF_6 to metallic uranium; however, the mechanics of these reductions are not well known. The thermodynamic properties of the materials involved show that the more common alkali and alkaline earth metals have substantial negative heats of reaction and negative free energy changes when used in the UF_6 reduction.

Although all of these materials should be investigated, sodium would probably be the best of this group as a reducing agent because of its low cost and easy handling due to low melting point, low boiling point, and low slag (NaF) melting point. The reaction would be $UF_6 + 6\ Na \longrightarrow U + 6\ NaF$.

Limited work has been done on several types of reactions: (a) high temperature vapor phase reductions,(5) (b) UF_6 vapor-liquid reducing agent reductions,(1) (c) vapor phase reductions in the presence of mercury vapor,(3) and (d) low temperature sodium-mercury amalgam reductions of UF_6 vapor.(7) The data indicate that the first two types of reductions should be given more emphasis than the last two because of the great difficulty experienced in the separation of uranium metal from mercury amalgams and quasis.

The Unit Operations Section should be able to determine the feasibility of this process and provide the necessary engineering information for design of a workable pilot plant.

The Chemical Technology Division has had some experience in low-temperature sodium reduction of UF_6 in the Metallex Program.(8) Some of the available data from the Hermex Program and other Metallex Studies(7) have possible application in this problem. Notable is the work done on the handling of materials and processing of uranium from mercury amalgams and quasis. The work done by Reid(3) on high temperature sodium reduction of $ThCl_4$ in presence of mercury vapor has limited application in a similar UF_6 reduction.

refs?

2.0 Objective

The object of this problem is to determine the feasibility of the direct and continuous reduction of UF_6 to metallic uranium by use of sodium or some other reducing agent and perform the necessary engineering development to make possible the design of a working pilot plant for this reduction. The feasibility of uranium metal recovery from the solid reaction residue and slag processing for residual uranium must also be determined.

3.0 Possible Methods of Solution

There are several alternate approaches to the solution of this problem. The reaction feasibility could be studied as a bomb reaction, a liquid sodium-UF_6 vapor reduction, or a vapor phase reaction. The bomb reduction and liquid sodium reduction would be less complex; however, they do not allow as much control and as much range of operating conditions as does the vapor phase reduction.

The continuous reduction mechanism and the uranium metal-slag separation could be carried out in one integrated system or broken up into two different segments. Isolating the two segments would allow closer control over each and thus facilitate the study of each.

The materials of construction and corrosion studies could be separated from the rest of the experimental work or they could be made an integral part of each operation. The later method would give actual operating conditions while the former method would allow more flexability and control.

Processing the NaF slag for residual uranium, if any, could be either a wet chemistry method or a molten salt-volatility type process.

4.0 Proposed Methods of Solution

It is proposed that the initial reaction feasibility be carried out in an experimental apparatus which would make it possible to study either the vapor phase reduction or the liquid sodium-UF_6 vapor reduction. This apparatus (see Fig. 1) would be a small, temperature and pressure controlled reactor which would contain either molten sodium blanketed with argon or vaporous sodium in equilibrium with a small amount of molten sodium. An entrance line will carry either pure UF_6 or UF_6 diluted with inert gas into the reactor at a calculated rate where it will react with the sodium. Temperature indicators and a remote sight glass will give an indication of the reaction and complete analysis of the solid residue will make it possible to determine

ORNL-CF-57-10-28

To be presented at the Second Winter Meeting of the American Nuclear Society in New York, New York, October 28-31.

THE PREPARATION OF THORIUM METAL BY SODIUM AMALGAM REDUCTION OF THORIUM CHLORIDE: THE METALLEX PROCESS

O. C. Dean and G. K. Ellis

Oak Ridge National Laboratory
Oak Ridge, Tennessee
Operated by Union Carbide Nuclear Company
for the Atomic Energy Commission

THE PREPARATION OF THORIUM METAL BY SODIUM AMALGAM REDUCTION OF THORIUM CHLORIDE: THE METALLEX PROCESS

O. C. Dean and G. K. Ellis

1.0 ABSTRACT

A process, developed at Oak Ridge National Laboratory, produced thorium metal by the continuous reduction of anhydrous thorium tetrachloride with sodium amalgam on a scale up to 3.5 pounds per hour. The salt was vigorously agitated with an excess of sodium amalgam which was produced by the electrolysis of aqueous sodium hydroxide. The resulting slurry of thorium mercuride in mercury was washed free from impurities and reaction by-products with dilute HCl and water. A solid concentrate of the thorium mercuride was prepared by filter-pressing the dilute slurry. The remaining mercury was removed by vacuum-distillation, resulting in massive metal of about 0.8 of the theoretical thorium density. The metal was fabricated into rods by direct extrusion or by arc-melting followed by extrusion.

2.0 NEED FOR THORIUM

Thorium, a fertile, non-fissionable material is readily converted to uranium^{233} by neutron absorption. U^{233} is a fissionable material of high potential value in the future power reactor economy because its nuclear properties are superior to those of U^{235} and it is easier to handle than plutonium.

The availability of thorium in nature is about the same as for uranium.

3.0 DESCRIPTION OF METALLEX PROCESS

3.1 Chemistry

The Metallex Process is a new thorium reduction process to produce reactor grade thorium metal. The basic feed material, thorium nitrate, is converted to hydrated thorium oxalate by contacting the nitrate with oxalic acid at 40°C. The oxalate is pelletized and chlorinated at 675°C to thorium tetrachloride.

The primary reaction for the reduction is $ThCl_4 + 4\ NaHg_4 + 60\ Hg \longrightarrow ThHg_3 + 4\ NaCl + 73\ Hg + 20$ kcal. Side reactions occur, especially in the presence of water and oxygen, which produce oxides of thorium and sodium and thorium oxychlorides.

Clean $ThHg_3$ is wetted and protected by excess mercury, while partially oxidized $ThHg_3$ separates from the mercury phase. The impurities not wetted by mercury, and residual-free sodium, are washed out by dilute HCl, then water. The product, a quasi amalgam of $ThHg_3$ suspended in mercury, about 1% thorium, is dried and consolidated by filtration, pressing, and retorting.

3.2 Function of Mercury

All steps of the process up to the final isolation of the metal from mercury are carried out at low temperatures, reducing equipment corrosion. Mercury is used to protect the highly pyrophoric thorium metal from oxidation during processing and serves as a process fluid having flow characteristics which make a continuous process possible.

3.3 Cost

Metallex may be operated at a processing cost of approximately $2.00 per pound. The estimate includes amortization of capital equipment but not the value of thorium nitrate.

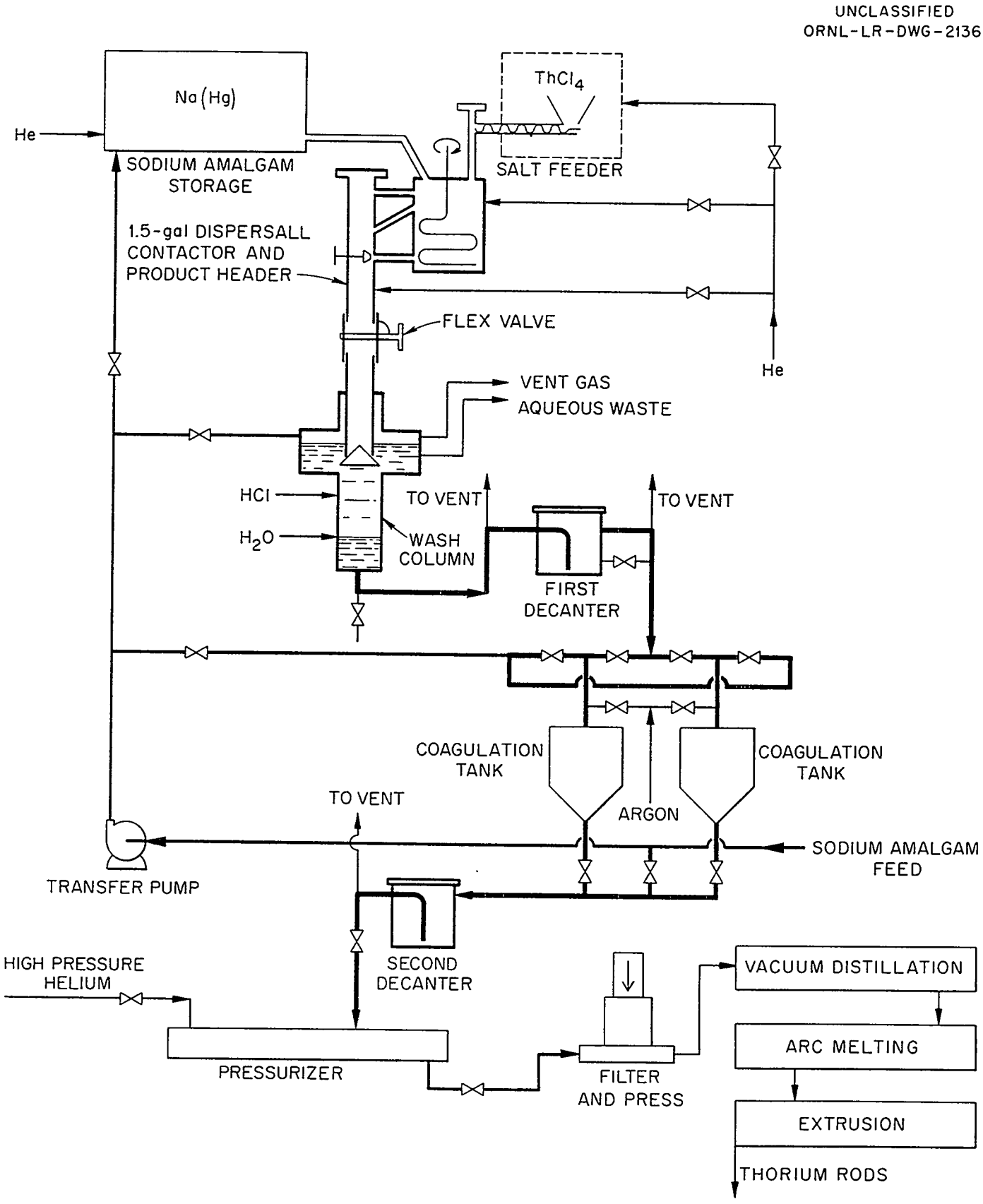
3.4 Continuous Process

A continuous process for the reduction of anhydrous thorium tetrachloride was designed, fabricated, installed, and successfully operated after a six-month period of component testing and revision.

The continuous process consisted primarily of a reduction and a washing step (Fig. 1). The thorium concentration operations were conducted batchwise and consisted of filtration, vacuum distillation, and arc-melting. An intermediate or coagulation period, occurred in 2-60 gal holdup tanks following the wash column. Two amalgamated nickel phase separators located on either side of the coagulation tanks removedlow density impurities from the quasi amalgam product. Development of a reduction step capable of being operated continuously was the primary concern of this engineering program.

4.0 DEVELOPMENT PROGRAM

The feasibility and chemistry of the process ~~was~~ were studied in the laboratory on a small scale (approximately 30 g of thorium per batch). Further development of the reduction and washing steps was carried out on a 1-kilogram thorium scale. Finally, continuous reduction and amalgam-washing were studied on a 3.5-lb thorium per hour scale. Isolation of the thorium metal by filter-pressing and vacuum distillation was carried out batchwise on a 10-g to 20-lb



Metallex Large Scale Thorium (3.5 lb of Th/hr) Production Process.

FIGURE 1

scale. The sponge metal product of vacuum distillation was extruded directly to rods in tests of 150-g billets, and several small billets were consolidated by direct extrusion. A 10-lb billet was made by non-consumable arc-melting of several small sponge billets.

In the continuous process, the most difficult problem, which was solved successfully, was the continuous discharge of the semi-solid quasi-amalgam product from the dry contactor to the water wash column while maintaining a dew-point in the contactor of -35°F.

5.0 COMPONENTS IN CONTINUOUS PROCESS

5.1 Reduction Contactor

Continuous reduction was accomplished in a 1.5-gal Dispersall, top drive unit (Fig. 2). A cup rotary type of impeller made of Hastelloy C coupled to a variable speed Reeves drive was used. Speed of agitation was varied from 865 to 1440 rpm and finally optimized at 1160 rpm.

5.2 Product Removal Header

The quasi product was discharged from the reduction contactor through an overflow line at a 45° angle into the header. A cross section of the header is shown in Fig. 3. A vertical drop through the header and product removal line into the wash column allowed maximum opportunity for product removal from the contactor. Flanged connections facilitated maintenance and blind flanges were conveniently located in the header to permit access for cleanout purposes.

5.3 Aqueous Wash Column

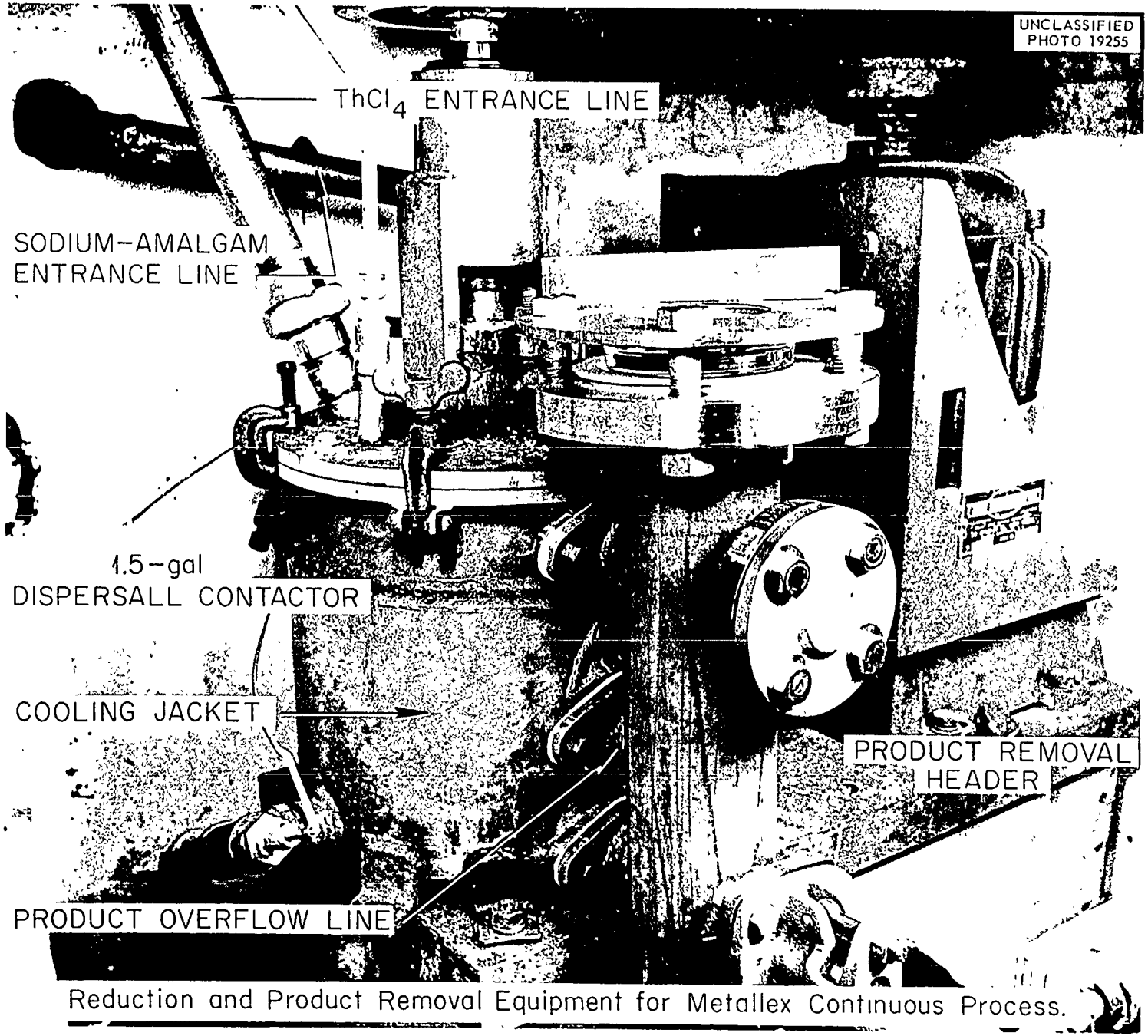
Countercurrent aqueous washing of the slurry product was achieved using a 6-ft long, 4-in. dia glass wash column vertically mounted directly below the header (Fig. 4). Unreduced thorium, NaCl and excess sodium were removed in the top 4-ft section by washing with 3 M HCl. Washing with demineralized water in the bottom section removed chlorides.

5.4 Gas Disengaging Section

A gas disengaging section to aid in elimination of approximately 6 cu ft/min (S.T.P.) of process off-gas was included in the top of the wash column. This gas was composed of hydrogen from the reduction reaction and helium. The helium originated in the inert gas blanket requirements for the process, and from purging down the plastic product line to minimize entry of water vapor into the reduction zone by turbulent mixing and back diffusion.

5.5 Deflector Cone

Throttling of the product removal line in the upper part of the wash column was effectively accomplished using a conical polyvinyl chloride plug



Reduction and Product Removal Equipment for Metallex Continuous Process.

FIGURE 2

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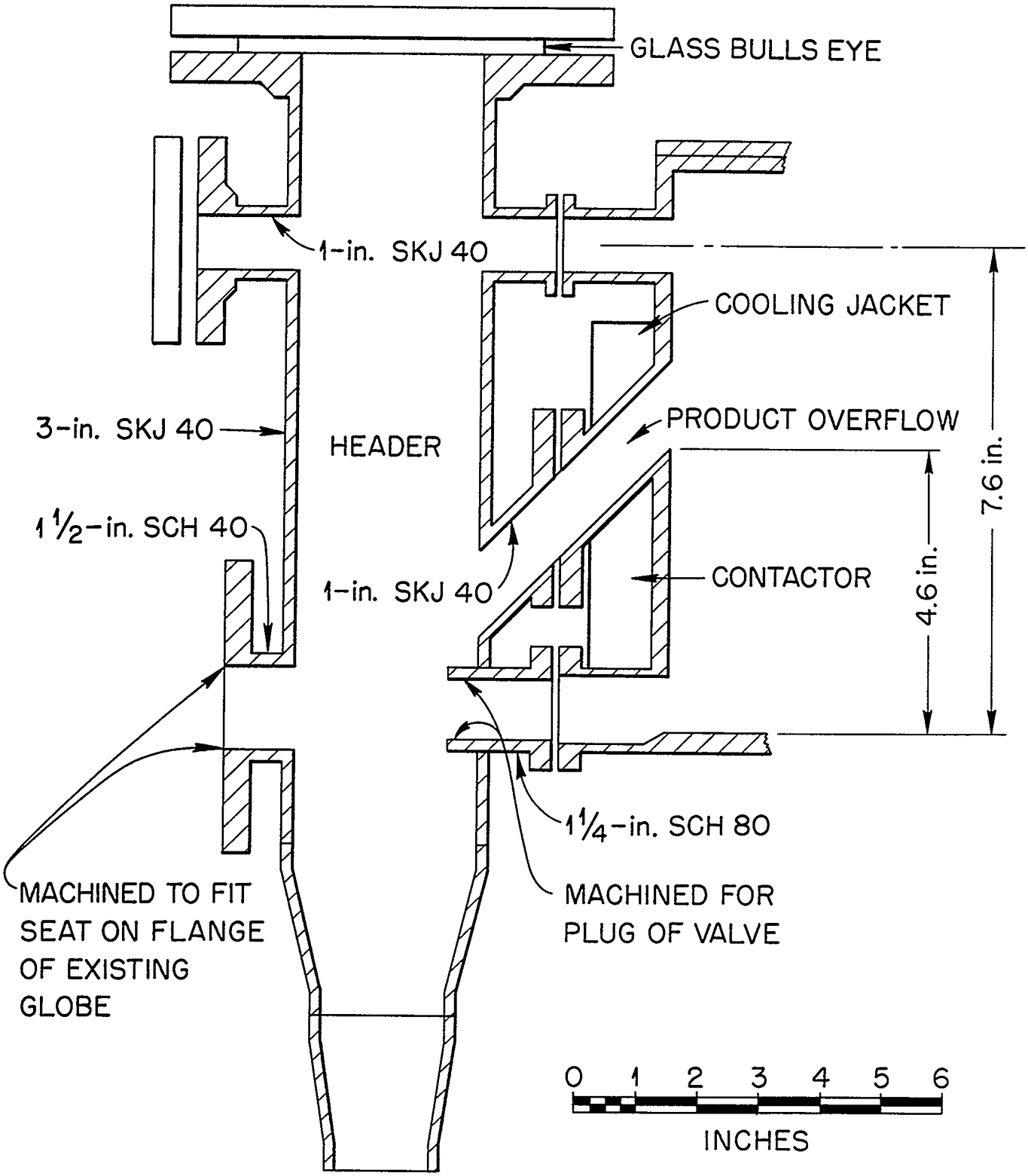
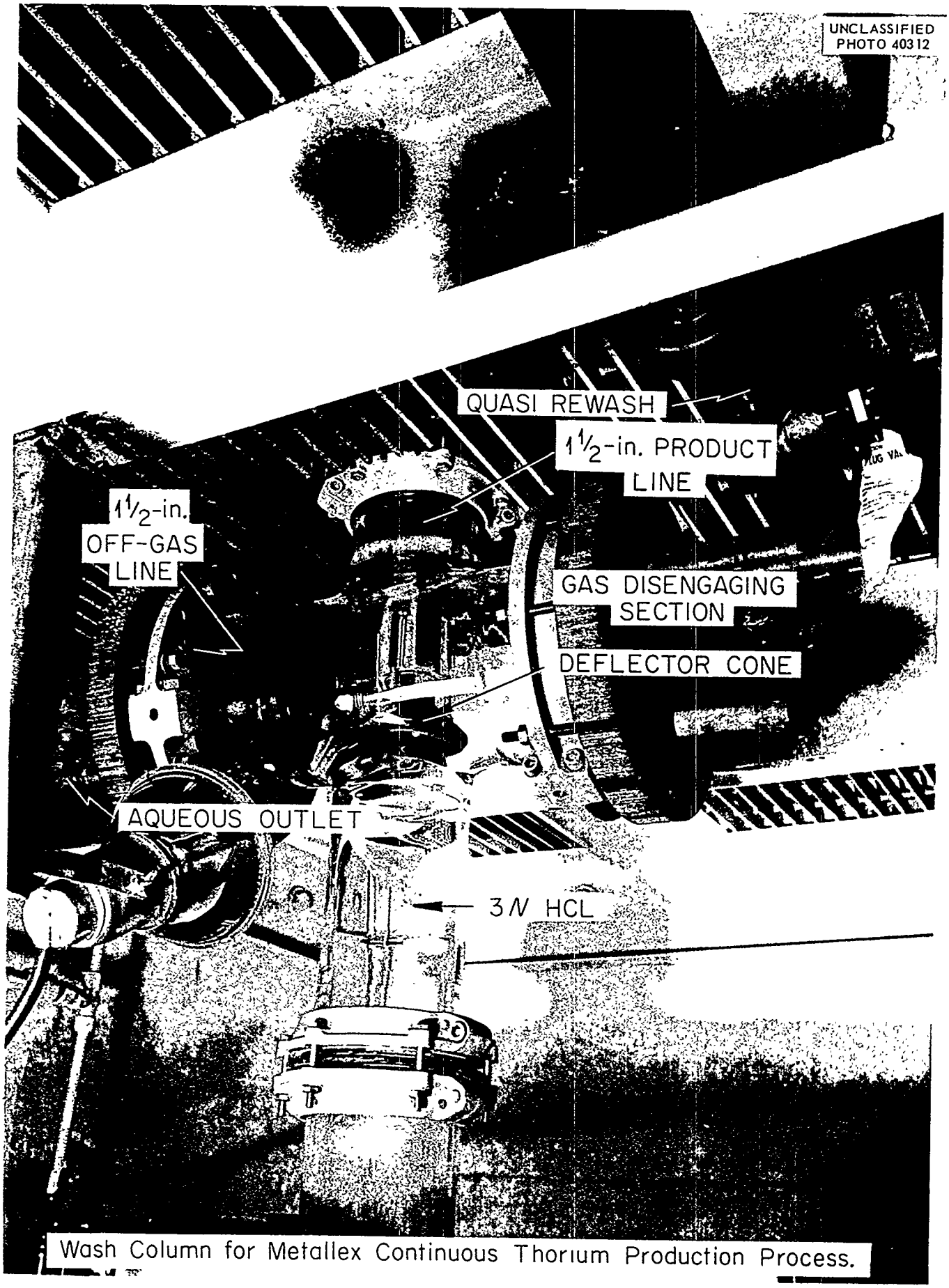


Metallex Withdrawal Header.
FIGURE 3



Wash Column for Metallex Continuous Thorium Production Process.

FIGURE 4

in the end of the product line (Fig. 5). This plug, capable of movement only in a vertical direction, was adjusted to give the least cross sectional flow area required for product removal. The cone served several purposes.

(1) Water vapor, tending to back up the line, was effectively purged from the line. Throttling of the product line with the deflector cone resulted in increased velocity and therefore purging effectiveness of helium and product through this constricted opening.

(2) The decomposition reaction was minimized in the line. In operation the cone projected above the water surface, decreasing the surface available for reaction. Also the reduced flow area served to decrease the product residence time by increasing the flow velocity at the point of aqueous contact.

(3) Interference of the sodium-water reaction with washing action in the column was decreased. Directed by the sloping sides of the cone, excess sodium amalgam was routed to a glass ledge in the upper part of the column where sufficient residence time was provided for the bulk of the sodium to decompose. The rest of the column then was used for washing the product.

5.6 Filter-Press and Vacuum Retort

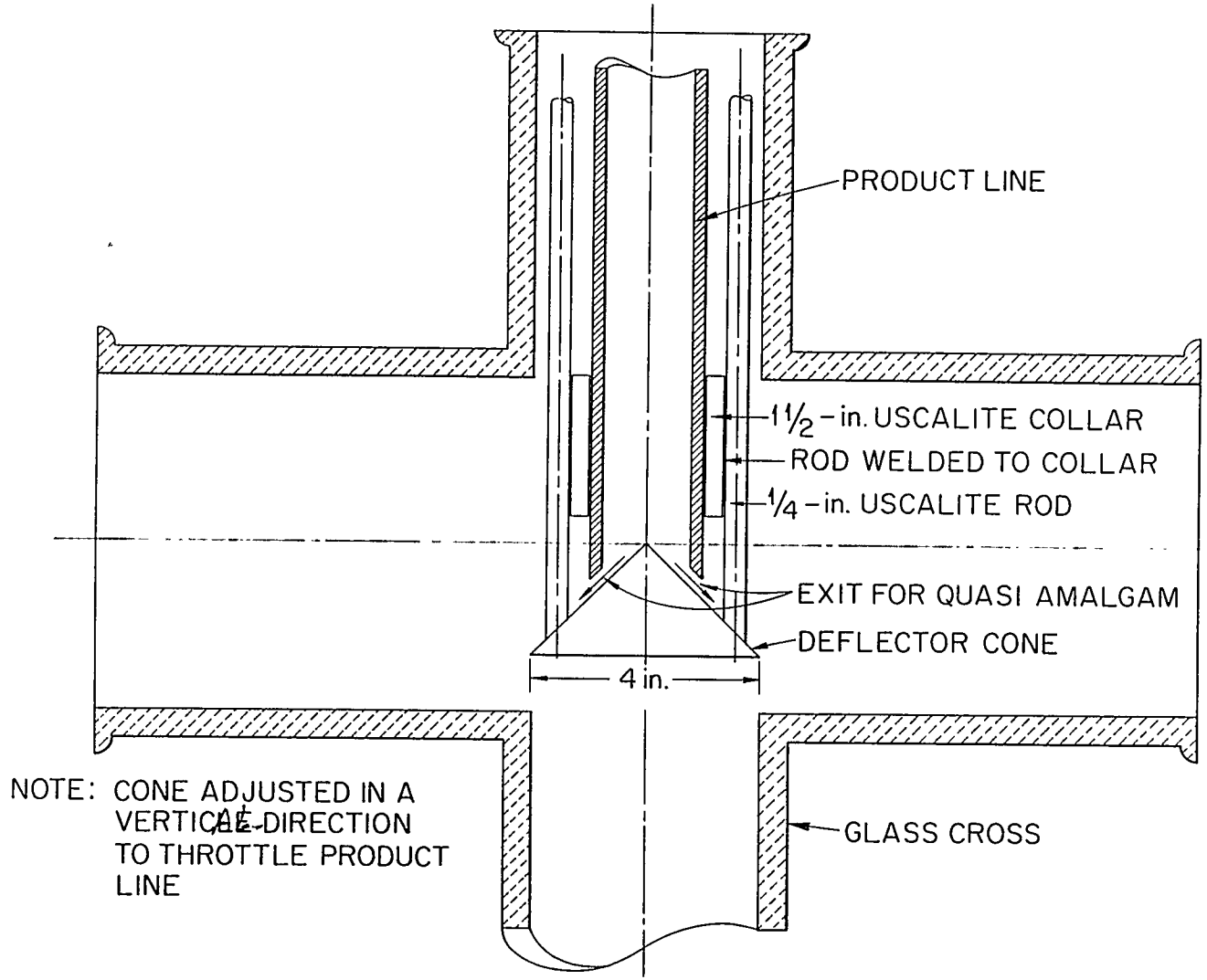
The filtration of the washed 1% thorium amalgam in a 5-in. dia Carver filter press removed 90% of the mercury. A 60-lb solid cake of $ThHg_3$ and excess mercury was produced containing about 15% thorium. Vacuum distillation of two of these cakes per batch in a steel retort removed the remainder of the mercury and produced integral solid billets of 65 to 85% of the theoretical density.

5.7 Amalgamated Decanter

Oxide content of the sintered thorium slugs, probably from water carry-over from the quasi-amalgam washing stage, was slightly greater than the allowable 1% in initial operation of the continuous process. Experiments performed on a small scale to investigate this result indicated that the oxide content of the final sponge could be decreased by any of several amalgam-washing procedures (Table 1). In the order of increasing efficiency for oxide removal, the following procedures were tested: further $HCl-H_2O$ washing, vacuum drying at 25°C, decanting of water from product using amalgamated vessels, heating to 100°C and skimming, and washing with various oxidation inhibitors.

Note that the experiment with an amalgamated decanter also provided one of the highest bulk densities, another desirable feature.

A significant feature which may be noted in Table 4 is that oxide content is directly proportional to voidage percent. It is suspected that voidage surfaces generated during mercury removal contain highly reactive thorium which readily combines with any available oxygen, either present in the atmosphere or in a water dispersion throughout the cake remaining from the washing and pressing operation.



(LOCATED IN UPPER PART OF WASH COLUMN IN LARGE SCALE CONTINUOUS PROCESS)

Deflector Cone Details.

FIGURE 5

Table 1 Effects of Amalgam Washing Procedure on the Quality of Sintered Thorium Slugs

Sources of amalgam: $ThCl_4$, batch reduced in 1-1/2 gal Dispersall mixer by sodium amalgam at 130°C; washed with 3 N HCl, then water in a 4-in. column

Scale: 10 g thorium

Average of 2 to 5 values in each case

Secondary Washing Treatment	Bulk Density (g/cm^3)	Voidage (%)	ThO_2 Content (%)
None	8.4	28	1.1
Further HCl-H_2O washing	8.4	28	0.9
Heating to 100°C and skimming	7.6	35	0.6
Vacuum-drying at 25°C	9.4	20	0.7
Decanting with an amalgamated decanter	9.4	20	0.7
Washing with oxidation-inhibitors*			
Versene	9.4	20	0.5
Aniline	9.5	19	0.6
Pyridine	8.6	26	0.6

* Followed by decantation to remove water.

Table 2 Properties of Sintered Metallex Thorium from Metallex Large Scale (3.5 lb Th/hr) Continuous Process, with and without Decantation

Conditions: Reduction, 130°C, 20-min residence time, 1160 rpm
Filtration-pressing, variable flow rates and pressures
Retorting, 25-1100°C continuous cycle in 12-hr period

Reduction Run	Billet Ident. No.	Thorium Metal Properties (ppm)						Bulk Density (g/cm^3)	Remarks
		ThO_2 (%)	Hg	Fe	Cr	Ni	C		
7	1	0.72	--	--	--	--	--	8.21	No decantor
8	2	1.21	--	--	--	--	--	9.65	No decantor
9	5	1.80	75	27	<25	<25	--	9.27	No decantor
10	10	0.38	10	1532	--	435	0.02	9.58	One decantor used
11	13	0.59	20	269	--	38	0.11	8.20	One decantor used

The procedure adopted in the continuous process to decrease oxide content of the sintered slugs was the installation of two amalgamated containers, functioning as decanters, immediately after the wash column. Following the addition of the first decanter (between Runs 9 and 10), sintered thorium slugs produced during Runs 10 and 11 contained thorium oxide over the range 0.38 to 0.68% (Table 2).

6.0 THE RESULTS OF OPERATION OF CONTINUOUS PROCESS

6.1 226-lb of Thorium Metal Produced

A total of 226-lb of thorium metal as $ThHg_3$ was produced in seven runs during 90-hr of operation (Table 3). The overall reduction yield was 82.5%; 2.5-lb Th/hr was the average product rate. Reduction was accomplished in a 1.5-gal Dispersall contactor with a 20-min reaction residence time at 130°C. A maximum production rate of 3.5-lb Th/hr was maintained over a 16-hr period in the last run, in which 18.5% sodium excess was used over that required for stoichiometric reaction.

6.2 Decrease of Production Rate with Time

A plot of rate of thorium reduction versus time for one essentially continuous 36 hr run is shown in Fig. 6. The thorium feed rate was gradually increased until the production rate for the last 16-hr period was 3.5 lb Th/hr. Notice the apparent decrease in yield with time for a given feed rate. Considering the difficulties of monitoring the amalgam stream this trend is not necessarily statistically significant. A representative sample of the characteristically heterogeneous quasi-amalgam slurry was difficult to obtain, and analysis for thorium was accurate to within $\pm$ 3%.

If significant, this trend could be caused by a slow buildup of reaction products in the reduction contactor which tended to slow down the reduction reaction.

The product of continuous reduction and amalgam-washing was a quasi-amalgam, approximately 1% thorium. In a 5-in. dia press with a sintered steel filter at one end, 90% of the mercury was eliminated to give a solid amalgam cake of ~10% thorium weighing about 70 lb. The remainder of the mercury was removed in a vacuum retort at 1100°C, resulting in a 7 lb billet having 65 to 85% of theoretical thorium density. Forty-two lb of metal were thus isolated, and had chemical properties shown in Table 2.

7.0 BATCH SCALE STUDIES OF PROCESS VARIABLES

7.1 Factors Affecting Overall Efficiency of Process

In order to find the range of operating conditions giving high reduction

Table 3 Thorium Production in Metallex Continuous Process

Conditions: 20-min residence time at 130°C ± 5°

Feed, $ThCl_4$, sublimed material containing less than .20% H_2O, Na-Hg, 2.5-3.8 M

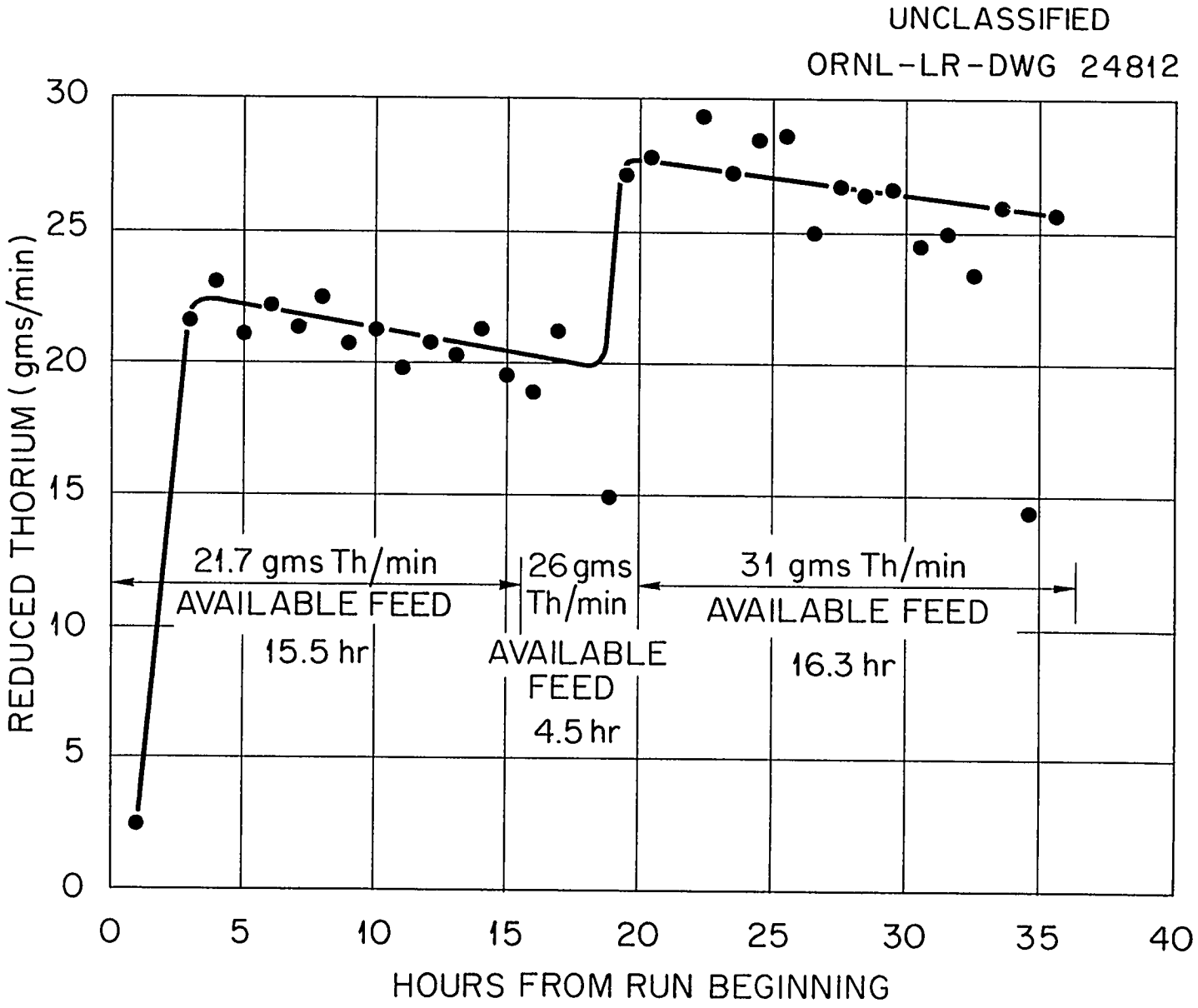
Contactor, 1.5-gal Dispersall top drive unit

Agitation speed, 1160 rpm

Run	Th Metal Produced (lb)	Duration of Run (hr)	Sodium Excess (%)	Reduction Efficiency (%)
7	7.07	5.0	89	66.4
8	25.5	12.75	variable	83.0
9	22.4	9.5	43	83.3
10	28.3	12.83	25	70.5
11	29.1	13.33	25	75.2
13	63	18.33	51 (avg)	92
14	50	18.0	18.5	87

Totals 225.4-lb 90-hr

Average Reduction.....82.5%



Thorium Production in Metallex Large Scale Continuous Process During Runs 13 and 14. (Run 14 was a continuation of 13).

FIGURE 6

yields, a series of reduction runs were performed on a batch scale, using the 1.5-gal Dispersall contactor as a reduction unit. Related studies were then made, taking this reduction product through the usual thorium concentration steps, to determine overall yields.

The factors in the reduction step affecting reduction yield, filtration recovery, and final metal quality were temperature, contact time and agitation rate. Figure 7 presents a family of curves of reduction yield vs. temperature at three different residence times. The same agitation rate and holdup volume is used. Notice that there is a maximum yield for each residence time. Also, as the residence times are decreased the maximum is displaced in the direction of higher temperature of reduction. This is more clearly shown in Fig. 8. For any given temperature there is an optimum contact time.

Note that a 20-min residence time for two liters holdup at an agitator speed of 1410 rpm was representative of a condition in which yields better than 85% may be expected over the range 130-180°C.

If maximizing the reduction yield were the only consideration in optimizing the process variables, this high temperature-low residence time would have been a good choice. However, this higher temperature operation had an adverse influence on the oxide content of the sintered thorium slug product of the process and decreased the particle size and recoverability of thorium by filtration.

7.2 Criterion for Optimization

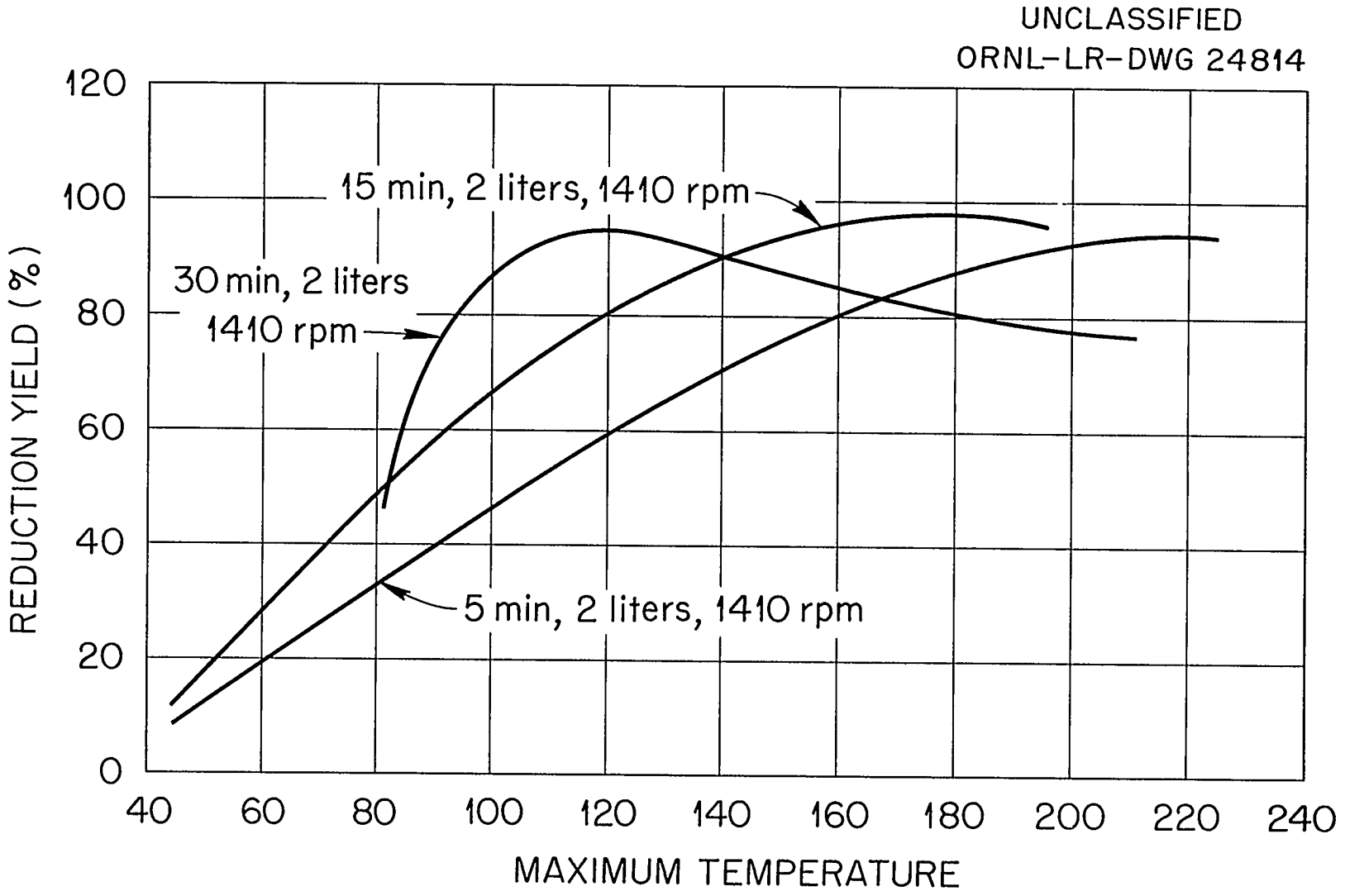
For either batch or continuous operation, the criterion for optimization was the obtaining of a maximum overall yield of specification grade thorium. Generally, this overall yield was adversely affected by any feature within the process which would either lower the overall quantity of yield or introduce impurities which would appear in the extruded product.

7.3 Causes for Thorium Oxide Increase above Specification

Laboratory results showed that thorium oxide content in the sintered slug was directly proportional to the reduction temperature, and the degree and time of agitation (Table 4). Run G at 125°C, 1100 rpm and 20 min residence time, showing an oxide content of 0.63%, was the only run having less than the specification oxide requirement of 1%. A high oxide content as a result of increase in temperature is shown by comparison of Runs B and D; for the same agitation rate and time, an increase from 180°C to 230°C in the reduction temperature increased the oxide content from 2.8% to 5.2%.

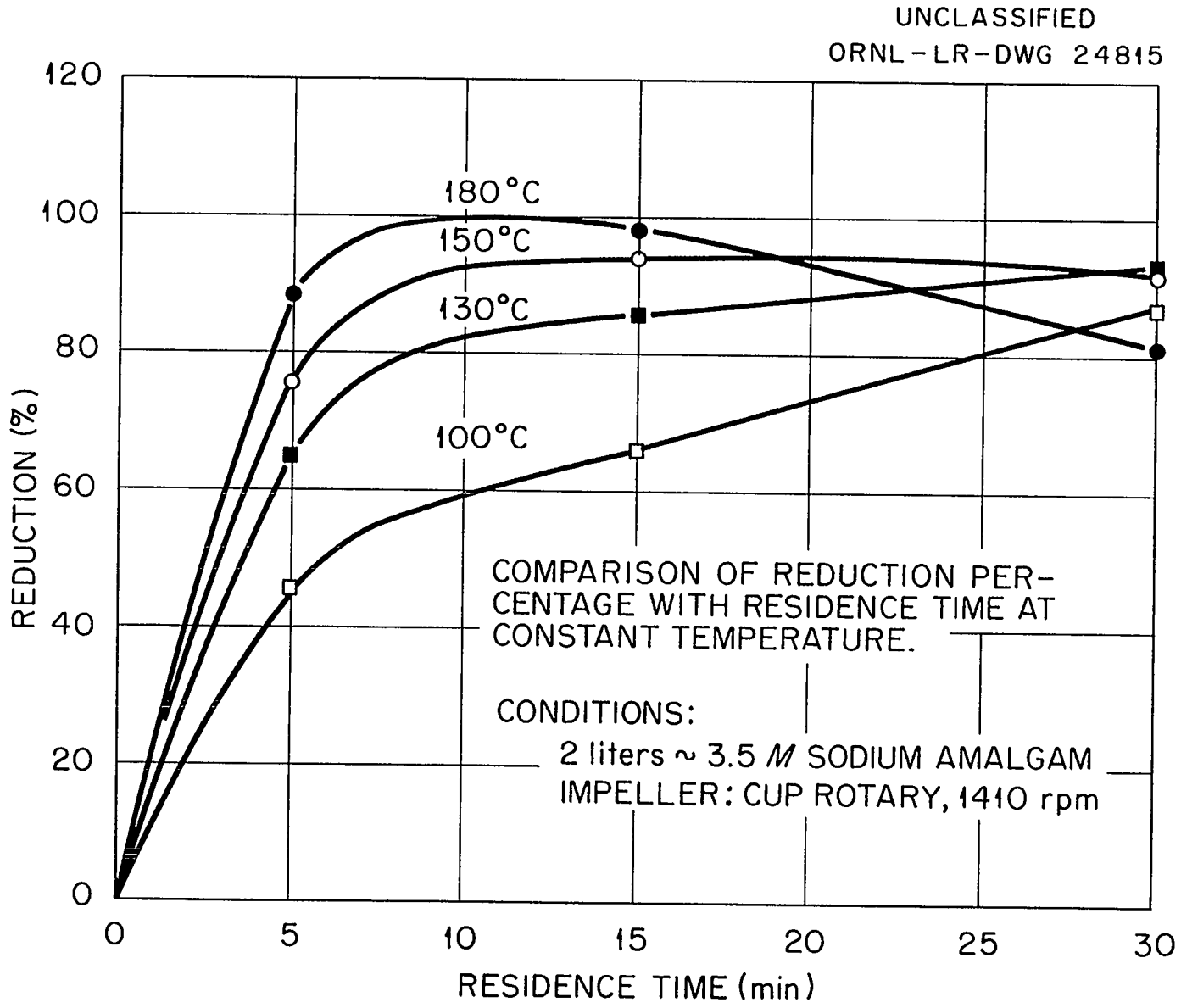
8.0 OPTIMIZATION OF PROCESS VARIABLES FOR CONTINUOUS PROCESS

Because of the formation of oxide and lowered filtration efficiencies present at higher temperatures, a reduction temperature of 130°C was chosen



Variation of Reduction Percentage with Maximum Temperature During Batch Operation Using a 1.5 gal Dispersall Contactor.

FIGURE 7



Reduction of $ThCl_4$ by Dry Salt Contacting During Batch Operation in a 1.5 gal Dispersall Contractor.

FIGURE 8

Table 4 The Effects of Reduction Variables on the ThO_2 Content of the Thorium Metal Product

Reduction accomplished in a 1-liter size Rushton contactor using 3.5-4 M NaHg.

Run No.	Reduction Temperature (°C)	Agitator Speed (rpm)	Agitation Time (min)	ThO_2 Content Sintered Th (%)
A	300	1450	90	6.75
B	230	2250	30	5.21
C	230	2250	5	1.95
D	180	2250	30	2.80
E	125	1500	35	1.70
F	125	1100	45	1.13
G	125	1100	20	0.63
H	125	1000	60	1.36
I	100	1500	120	1.20

for continuous operation. In this choice, recognition was also made of the more severe materials limitations at higher temperatures of equipment in contact with corrosive amalgams and aqueous HCl solutions.

Optimum conditions for reduction on a batch scale were assumed to be identical with those for continuous operation. For continuous operation, a 20-min residence time was chosen as representative of a condition for batch operation in which yields greater than 85% may be expected over the range 130-180°C (Fig. 8).

Data for batch operation at different holdup volumes indicated reduction efficiencies to be essentially independent of holdup volume over the range 2-4 liters in the 1.5-gal Dispersall contactor. A 3.5-liter holdup was chosen for continuous operation, dictated by the geometry of the 1.5-gal Dispersall unit. Choice of residence time and holdup volume determined a sodium amalgam flow rate of 175-ml/min.

Referring again to Table 4 the 50% higher oxide content of Run E compared with Run F can be explained in terms of the increase of agitation rate from 1100 to 1500 rpm. From this criterion, a relatively low agitation rate of 1160 rpm was chosen for the continuous process.

The average of 82.5% and the maximum of 92% reduction efficiency obtained during operation of the continuous process confirmed a satisfactory choice of the process variables. The average reduction efficiency agreed rather well with the batch results shown in Fig. 8.

9.0 FEASIBILITY OF BY-PASSING ARC-MELTING STEP

Although it may be possible to consolidate the sponge billet to rod by direct extrusion, the procedure more likely to produce specification metal is consumable arc-melting of several billets heliarced together.

Direct extrusion without arc-melting produced metal of acceptable rolling and drawing properties. However, the metal had a slightly high oxide content and a low tensile strength compared with reactor grade specifications.

Chemical, physical and metallurgical properties of six thorium rods prepared by the hot-extrusion of sintered Metallex billets without intermediate arc-melting are compared with specifications in Table 5. The 1-1/8-in. dia billets were prepared by batch reduction of $ThCl_4$ in the Dispersall unit, amalgam-washing, filtration, pressing and vacuum-retorting. The high ThO_2, carbon and H were attributed to contamination during hot-extrusion due to the use of a dag die lubricant. Iron contamination in two specimens was probably due to incomplete washing of chlorides from the amalgam. Low tensile strength and elongation values suggested that voids in the metal did not knit during extrusion. Therefore, it was considered unlikely that by-passing the arc-melting step would be feasible.

Table 5 Properties of Metallex Thorium Rods from Direct Extrusion of Sponge Billets

Metal prepared by batch reduction of $ThCl_4$ in the 1-1/2 gal Dispersall mixer.

Reduction Conditions: 100-220°C, reduction temperature
2 liter, holdup
1410 rpm, agitation speed

Property	Range	Specification
Density, g/cm^3		
Initial compact	6.9-9.1	-
Extruded rod	11.2-11.7	11.6
ThO_2, wt %	1.4-2.6	1.0
C, wt %	0.03-0.36	0.04
H, ppm	36-87	.10
N, ppm	9-30	50
Fe, ppm	30-3020	100
Hg, ppm	10-170	40
Tensile strength, psi	15,100-19,000	31,500
Elongation, %	10-20	35
Vickers Hardness No. (1 kg load)	45-64	60

10.0 ACKNOWLEDGMENTS

Others at the Oak Ridge National Laboratory beside the authors who have made substantial contributions to this program are: E. S. Bomar and J. H. Terry of the Metallurgy Division and J. C. Bresee, C. P. Johnston, R. O. Payne and J. C. Suddath of the Chemical Technology Division.

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CONTENTS

1.0 INTRODUCTION

Recent work at ORNL has been directed toward the development of a new reprocessing method, the Hermex Process, in which mercury is used as a dissolvent or extractant for purifying and recycling metals. Initial experiments have explored the feasibility of removing fission products from irradiated uranium and the recycle of scrap uranium in feed materials processing. The process will also be applied to thorium, zirconium, niobium, molybdenum, and aluminum as well as their alloys with uranium.

Several criteria have been established which may offer significant cost advantages over the presently used aqueous processing and the proposed pyrometallurgical method. The criteria for aqueous methods are the retention of uranium in the metallic state throughout the process and a more radiation resistant dissolvent and extractant. These criteria for pyrometallurgical methods are a low dissolution temperature, high purification, continuous process, and the use of standard materials of construction. Preliminary investigations indicate that the Hermex Process satisfies all of these criteria.

The basis of the Hermex Process is the solubility of uranium and other metals in mercury. After the mercury dissolution, the impurities and fission products are removed by slagging and washing the metal-mercury solution with solvents, and the purified metal is recovered by volatilization of the mercury and melting or sintering the high melting metal. Initial laboratory work on uranium has established the dissolution rate of solid uranium in boiling mercury. Later experiments showed that significant fission product removal was accomplished by slagging and washing the uranium-mercury solution that was obtained by dissolving sections from 3-year decayed X-10 reactor slugs. Scrap uranium metal from Fernald Feed Materials Preparation Center was shown to dissolve rapidly in boiling mercury without any preliminary cleaning or pickling. The Hermex Process offers considerable promise in the scrap recycle program because it can handle small scrap which is difficult to remelt directly and can probably purify this scrap without the expensive oxidation, solvent extraction, and reduction cycle.

2.0 SUMMARY

The Hermex Process is a new method for decontaminating irradiated metals and purifying scrap virgin metals. The process as applied to irradiated uranium consists of the following steps (Fig. 1).

1. Uranium is continuously dissolved in boiling mercury (356°C).
2. The hot 0.2% uranium-mercury solution from the dissolver vessel is withdrawn continuously leaving a slag layer containing ~ 87% of the fission products or impurities.
3. The 0.2% uranium-mercury solution is cooled to 25°C and concentrated to 3% U by vacuum filtration. The mercury filtrate is recycled to the dissolver vessel.
4. The 3% uranium quasi-amalgam is washed with dilute HCl to remove ~6% of the fission products or impurities.
5. The mercury is volatilized from the quasi-amalgam and the uranium melted to dense metal by slow heating to 1250°C in a single operation.

Rapid dissolution rates of 12-17 and 7-9 mg/min/cm^2 were obtained on massive unirradiated and irradiated uranium samples, respectively. About 1-5% of the uranium was lost to the slag and 2-3% in the aqueous wash. The uranium loss figures are not particularly significant as yet since they were controlled by the equipment used rather than process principles. Decontamination factors of 100-200 for gross γ and 400-500 for gross β activity were obtained in two experiments using X-10 uranium cooled about 3-years. The uranium product from these experiments had about twice the γ activity and 2/3 the β activity of natural uranium.

3.0 PROPOSED APPLICATIONS

Mercury appears to have many advantages as a metal reprocessing reagent. These include the ability to dissolve, degrade, or amalgamate most metals,

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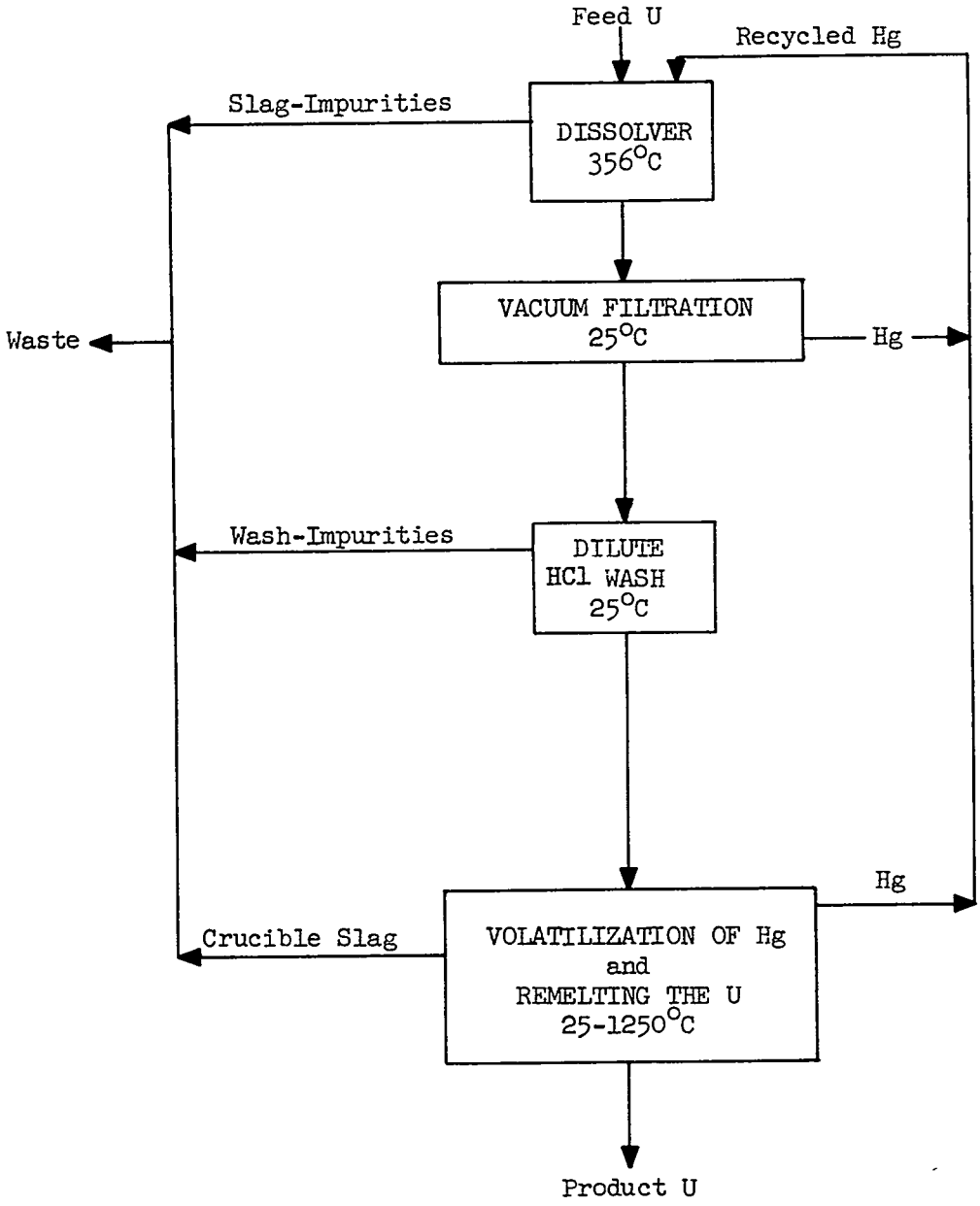

Fig. 1 Hermex Process

low melting and boiling points, radiation stability, and relative chemical inertness to nonoxidizing chemicals (such as hydrochloric acid). A program is now underway to evaluate a number of applications for mercury as a metal reprocessing reagent for dissolution, extraction, or degradation. Each of the cases described below would apply to either irradiated metal or to virgin or decontaminated metal in the fabrication plants.

3.1 Metal Dissolution

Uranium Metal

Massive uranium dissolves rapidly in boiling (356°C) mercury to the extent of 1 wt. %. R. G. Wymer derived the following rate equation from batch dissolution data:

$$\frac{dc}{dt} = \frac{-k\ s}{m}\ (c_s - c)$$

where c = uranium concentration in $\frac{\text{moles}}{1000\ \text{gm Hg}}$

$$k = \frac{2.2\ \text{gm Hg}}{\text{cm}^2\ \text{min}}$$

s = surface area of metallic uranium in cm^2

m = mass of the mercury in grams

c_s = apparent saturation concentration of uranium (0.94 mole % U) at 356°C.

R. G. Wymer's value of the saturation concentration of uranium in mercury is only 0.94 mole %. This does not agree with the value of 13 mole % given by Frost[1]. However, Frost prepared his uranium quasi-amalgams under special conditions, i.e., hydriding the uranium to form a powder, high temperature decomposition of the hydride, and dissolution of the finely divided uranium thus formed in heated mercury. The uranium-mercury phase diagram taken from Frost's paper is shown in Fig. 2.

Since a high concentration of uranium in mercury is desired, and the use of pressure equipment is probably impractical for preliminary laboratory

(1) Frost, B.R.T., Journal Institute of Metals, May, 1954.

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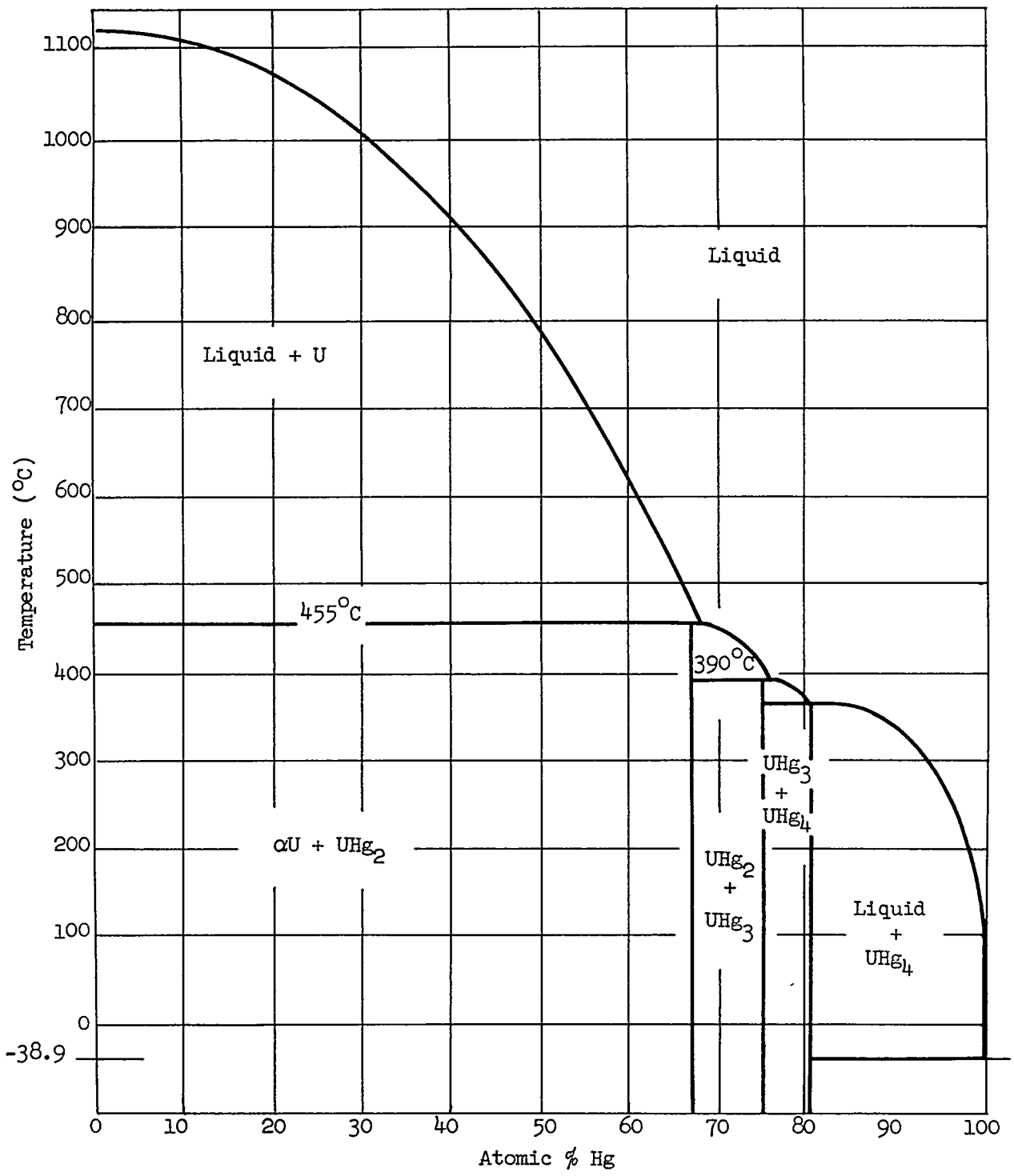

Fig. 2 The System U-Hg Showing Critical Alloys
(From: AERE M/R 1208, B. R. T. Frost)

work, a continuous dissolving technique was developed for use at the boiling point (see Section 4.1). In this procedure, dilute uranium amalgam is continuously withdrawn from the dissolver, UHg_4 precipitated by cooling, the mercuride recovered by filtration or centrifugation, and the mercury filtrate recycled to the dissolver (see Fig. 1). Insoluble impurities rise to the surface of the amalgam as a slag and are drawn off directly from the dissolver or are flushed away along with amalgam soluble impurities in a subsequent step in which the amalgam is washed with hydrochloric acid. Uranium amalgam is not decomposed significantly by hydrochloric acid in the absence of oxygen. The purified uranium amalgam is then sent to a retort where the mercury is volatilized off and the uranium melted to massive metal.

At the present time, recycle uranium metal is dissolved in acid, purified by solvent extraction, converted to salt and reduced back to metal. It appears that many chemical costs could be avoided using the Hermex process since the uranium remains in a semi-metallic state and does not require oxidation and reduction. In the case of irradiated metal, long cooling prior to processing would not be required thus avoiding excessive inventory costs. If the decontamination achieved is high, as is indicated by initial experiments, the subsequent metallurgy step could be classed as semi-remote since U^{237} would be the only significant activity remaining. In the case of other proposed pyrometallurgical schemes, decontamination factors are low and truly remote metallurgy is mandatory. If further decontamination is required by solvent extraction, the uranium can be recovered from the amalgam by oxidative leaching, i.e., treatment with oxygen and hydrochloric acid, and passed into the extraction cycle.

Uranium Alloys

It is expected that U-Zr, U-Nb, U-Mo and U-Al alloys will be dissolved or amalgamated by boiling mercury particularly in the case of alloys with high uranium contents. A dissolution rate of 5 $mg/cm^2/min$ for 98% U-2% Zr alloy has been obtained. Zirconium mercurides are known and aluminum is

readily soluble in mercury. The alloys are expected to act in the same manner as the pure metals. Thus the purification and recovery steps would be similar to those described above for uranium.

In some cases, the separation of macro amounts of metals may be practical. For example, metals such as aluminum, the alkaline earths, and the alkali metals which have relatively high solubilities in mercury at room temperature may be separated from metals with low solubilities, such as uranium and thorium by filtration or by a non-oxidizing acid wash. The insoluble metals are present as colloidal solid mercurides which are not decomposed by hydrochloric acid as are the Group I and II amalgams.

3.2 Metal Extraction

Mercury will be evaluated as a metal solvent for the recovery and decontamination of metals from fused salt solutions or molten metal reactor fuels. Heterogeneous reactor fuels are readily soluble in fused fluoride or sulfate salts. In this case, the transfer of the metals to the mercury phase would involve the simultaneous reduction of the metal; the presence of a reducing agent, such as sodium, in the mercury phase would be required. Extraction of metals from a molten metal fuel would not require a reducing agent, however. Many of the proposed operations would require pressurized containers in order to achieve high temperatures. Fortunately, industry has solved many of the implied operating problems in applications of high temperature mercury equipment in the turbine and oil cracking industries.

3.3 Degradation

Mercury can be used as a degrading vapor at high temperatures and atmospheric pressure to transform heterogeneous fuels to mercurides at elevated temperatures as an initial processing step prior to Hermex or aqueous solvent extraction processing. Experiments have shown that tantalum wire exposed to mercury vapor at 1200°C is degraded and can be readily powdered on cooling to room temperature. Pietrokowsky(2) has shown that zirconium mercurides are formed by mercury vapor and zirconium metal at 1000°C. The formation of hydrides prior to mercurization will also be

(2) Pietrokowsky, P., Journal Institute of Metals, Feb., 1954.

explored.

3.4 Reactor Processing

The use of mercury as a solvent for fuels in a fast breeder reactor has been proposed by F. L. Culler. Continuous processing of this type of reactor fuel appears feasible using Hermex Process principles. A schematic diagram of the proposed reactor and reprocessing cycle is shown in Fig. 3. Fuel from the reactor would pass through a clone or centrifuge to remove the insoluble fission products as a slag and the soluble fission products then removed by acid washing. Oxygen could be added prior to centrifugation to aid in slag formation if necessary. In this method of recycle the bulk of the uranium is recycled directly to the reactor and only a small portion withdrawn with the slag for complete decontamination and eventual recycle to the reactor.

The reactor conditions are chosen from phase diagram data and correspond roughly to the uranium concentration present in the Detroit-Edison Breeder reactor. R. A. Charpie has stated that the fast neutron cross section data for mercury must be rechecked before the practicality of the mercury reactor can be judged.

4.0 EXPERIMENTAL RESULTS

A total of four runs were made to study the Hermex Process as applied to uranium metal, two using unirradiated uranium to perfect the equipment, and two with 3-year cooled X-10 slug samples. A brief description of the actual procedure followed in each step of the Hermex process follows.

4.1 Uranium Dissolution

A photograph of the laboratory continuous dissolver is shown in Fig. 4. A 50 gram sample, 3/16" x 1" diam., of uranium was boiled (356°C) in 150 ml of mercury for 30 min under an argon atmosphere. Approximately, 140 ml of mercury containing 0.2 wt % uranium was dropped to the filter where it was allowed to cool to room temperature. A fresh portion of mercury was

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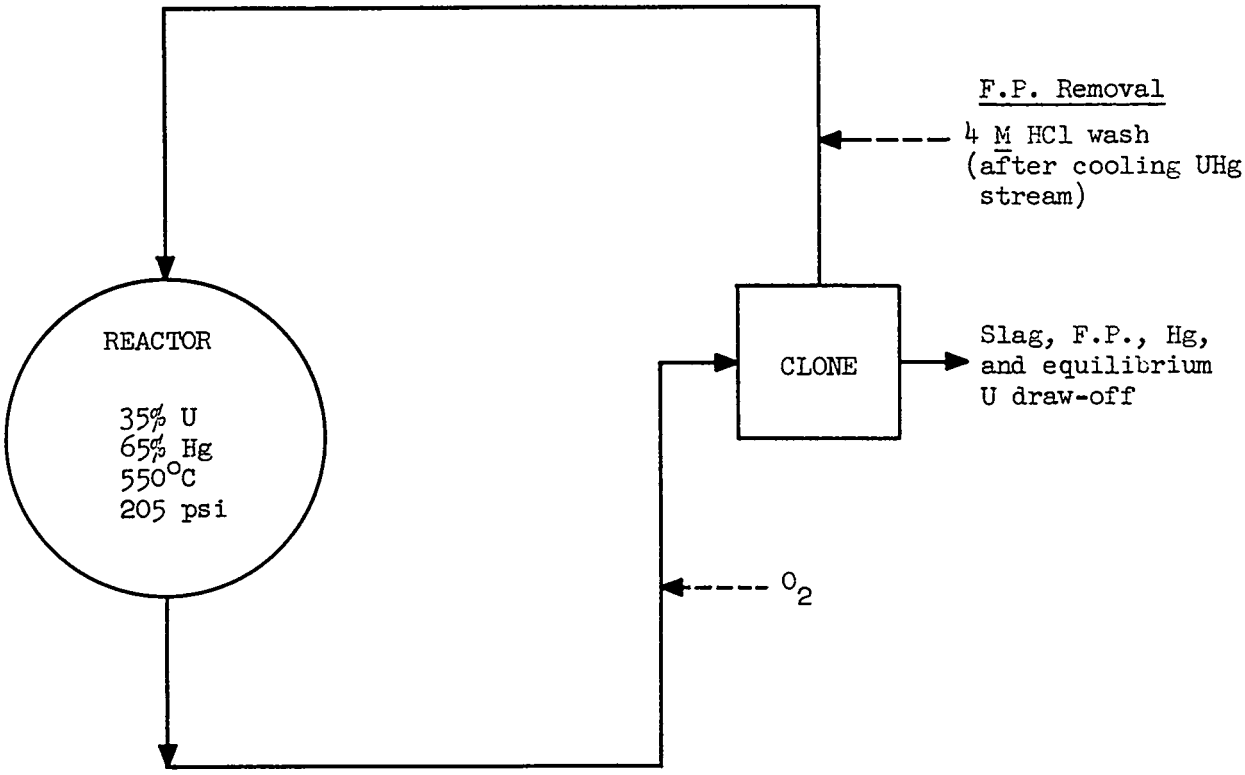

(Dotted lines indicate alternate or additional steps.)

Fig. 3 Hermex Reprocessing Scheme for a Mercury-Uranium Fast Breeder Homogeneous Reactor

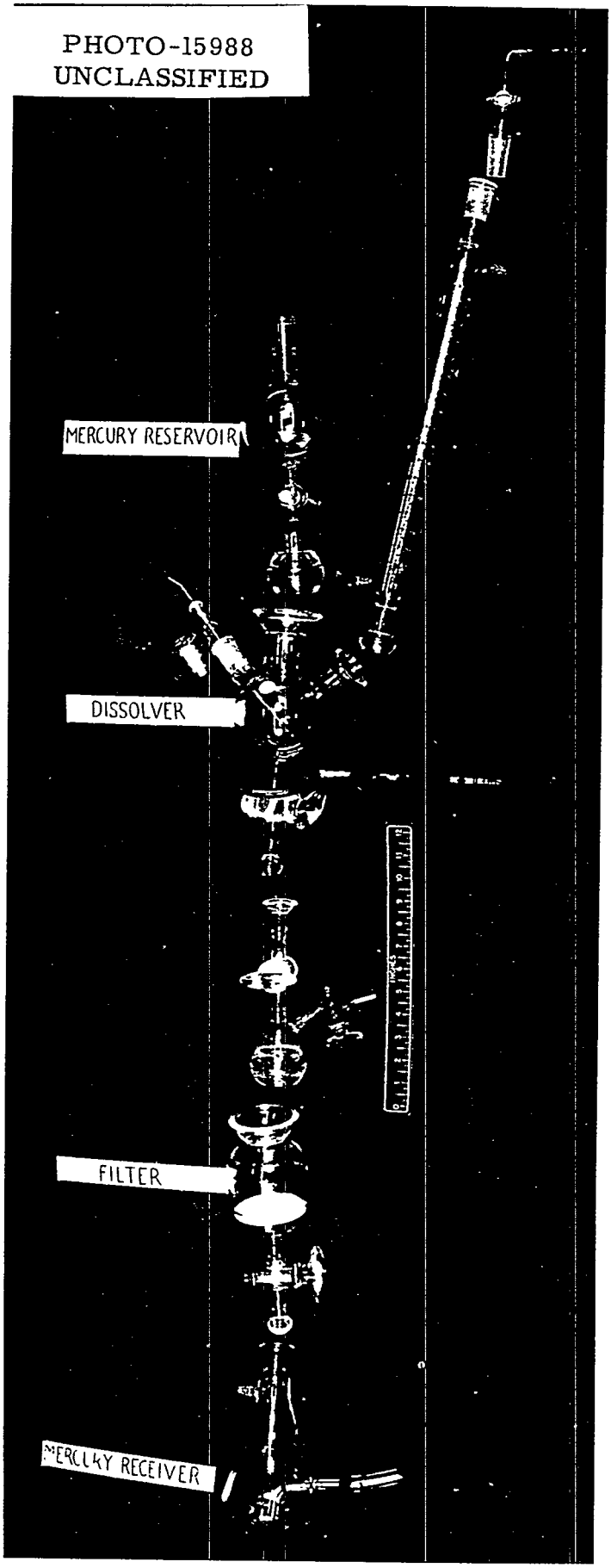

Fig. 4 Apparatus for Continuous Dissolution of U in Hg

immediately added to the dissolver from the mercury reservoir. After cooling, the uranium mercuride semi-solid, which formed as a suspension in the mercury phase, was recovered quantitatively by filtration. The mercury filtrate contained ~10 ppm uranium and was recycled from the mercury receiver to the mercury reservoir. A butter like uranium quasi-amalgam containing about 3 wt % uranium was retained on the sintered glass filter. The dissolution-filtration cycle was repeated about five times in each run to provide about 20 g of dissolved uranium for subsequent operations.

A film of black material, probably UO_2, was always observed on the surface of the mercury in the dissolver vessel after each run. This film was not unexpected because uranium dissolved in mercury is very pyrophoric and traces of air leaked into the system during the manipulations. About 5% of the uranium was lost as oxide in the first run but improved technique reduced this to 1% in the second run. About 4% of the uranium was lost in runs three and four.

Dissolution rates averaged 15 mg U/cm^2/min in the runs with unirradiated uranium and 8 mg U/cm^2/min in the runs with irradiated uranium (see Table 1). The rate of 15 mg U/cm^2/min is in good agreement with the rate of 20 mg U/cm^2/min obtained by Wymer in batch experiments. No reason for the lower rate with irradiated uranium can be offered at the present time. However, the mercury dissolution rates are higher than the average rate for uranium dissolution in nitric acid, i.e., 5 mg U/cm^2/min in 6 M HNO_3.

4.2 Acid Washing

The uranium-quasi amalgam retained on the filter was washed with five 100 ml portions of 1 N HCl and then dried with methanol. Efficient contacting was difficult because of the density of the quasi-amalgam. Nevertheless washing was continued until all visible particles of oxide were removed from the amalgam. Uranium losses were 2% to 3%.

4.3 Uranium-Mercury Separation

The uranium-quasi amalgam was loaded into an alundum crucible which

Table 1

Dissolution of Uranium in Boiling Mercury

Temperature - 356°C

Uranium Sample - 3/16" x 1" diam. section from X-10 slug*

Run No	Type of U	Dissolution Rate (mg U/cm^2/min)	U loss in slag (% of U dissolved)
1	Unirradiated	12	5
2	Unirradiated	17	1
3	Irradiated	7	5
4	Irradiated	9	3

*The Al jacket was removed prior to processing.

was then suspended in a vertical resistance furnace (see Fig. 5). This furnace was continually flushed with purified argon to exclude air during the heating cycle. The furnace temperature was slowly increased to 1250°C to boil off the mercury and melt the uranium. The condensed mercury distillate contained only one ppm of uranium. After cooling to room temperature a button of uranium was removed from the crucible. Some oxidation of the uranium during the heating cycle was inevitable and from 5-10% of the uranium was converted to oxide during this operation. More elaborate equipment and the processing of larger quantities to increase the volume to surface ratio of the uranium would reduce this oxidation loss. The mercury content of the uranium button was 10-30 ppm.

4.4 Fission Product Distribution

In the 3rd and 4th runs, sections of 3-year cooled uranium from X-10 reactor slugs were processed in the same manner as the cold uranium described above. A comparison of the radioactivity of the uranium before and after processing shows that overall average gross decontamination factors of 160 and 455 were obtained for γ and β activity, respectively. Individual β D.F.'s for run 4 were Cs-220, Sr-1100, TRE-800, Ru-7, and Pu (α)-6 (see Table 2). The Ru, Zr, and Nb D.F.'s are not considered significant due to their low specific activities in the initial sample. The lower D.F. for Pu is interesting since it corresponds to the lower values obtained in oxide slagging experiments on molten uranium metal at Argonne and North American Aviation. The specific gross β and γ activity of the purified uranium metal was about 2/3 and 3-1/2 times that of natural uranium, respectively (see Table 3).

About 86% of the gross activity was removed in the dissolver slag, $\sim$ 6% in the aqueous wash (see Table 4), and 0.4-3.0% in the crucible slag. The conversion of these numbers to decontamination factors per stage is impractical because the activity of the wastes from each stage and not the products was measured. Since the material balances are poor, calculations

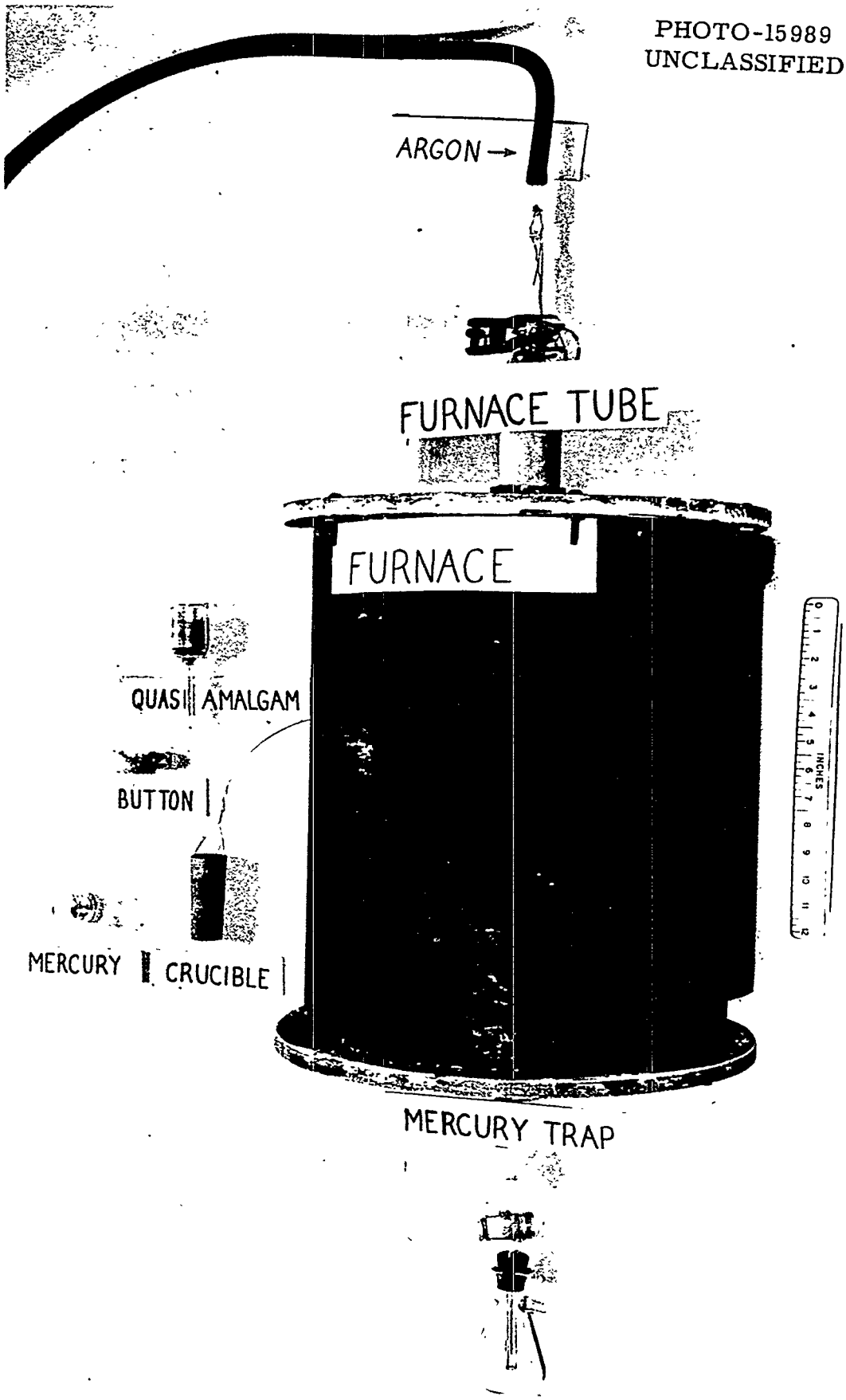

Fig. 5 Equipment for Separation of U and Hg

based on the difference between the waste activities and the product activities per stage are inaccurate. This method of calculation would show D.F.'s of 4-7, ~ 2, and 1.5-30 for the dissolver slagging, acid wash, and remelting steps, respectively. The most accurate and signifcant decontamination numbers are the overall values per gram of uranium shown in Table 2.

The mechanism of the dissolver slagging operation is not known but could be the result of insoluble fission products rising to the surface in the molten amalgam or a scavenging of the fission products by oxide impurities or a combination of both.

The efficacy of the acid wash as a separate decontamination step, rather than to merely remove oxide particles not properly separated in the slagging operation, has not been clearly established. However, no significant change in the ratio of fission product activities in the irradiated uranium and in the wash solution was noted. The ratio of Sr:Cs:TRE:Ru was 26:32:42:0.1 in the initial metal and 25:31:43:0.2 in the wash solution (see Table 5). Apparently, no element was selectively removed in the acid wash although this conclusion requires verification on higher activity samples where the accuracy of the results would be more significant. A black, insoluble material was flushed away from the quasi-amalgam in the acid washing step. This material may have been entrained in the dilute amalgam which was drained from the dissolver, or it may have formed by oxidation during the washing step.

Decontamination during the remelting step could be viewed as either a continuation (i.e., a 2nd stage) of the dissolver slagging operation or oxide scavenging as observed in regular pyrometallurgical procedures.

Table 2

Decontamination Factors for Irradiate Uranium Purified by the Hermex Process

Activity	Initial U c/min/g U		Decontaminated U c/min/g U		Decontamination Factor	
	Run 3	Run 4	Run 3	Run 4	Run 3	Run 4
gross γ	3.7×10^{7}	3.7×10^{7}	4.0×10^{5}	1.7×10^{5}	100	220
gross β	2.8×10^{7}	2.7×10^{7}	5.6×10^{4}	6.5×10^{4}	500	410
Cs β	9.3×10^{6}	9.2×10^{6}	6.3×10^{3}	3.3×10^{3}	1500	2800
Sr β	7.0×10^{6}	3.0×10^{6}	1.6×10^{4}	2.8×10^{3}	440	1100
TRE β	1.1×10^{7}	1.2×10^{7}	1.2×10^{4}	1.5×10^{4}	920	800
Zr γ*	----	5×10^{4}	2×10^{4}	2×10^{3}	---	10*
Nb γ*	----	1×10^{5}	2×10^{4}	8×10^{3}	---	25*
Ru β*	3.7×10^{4}*	2.7×10^{4}*	1.4×10^{4}	2.6×10^{4}	3*	NiL*
Pu α	1.3×10^{6}	1.3×10^{6}	2.9×10^{5}	2.9×10^{5}	4	7

*Data not significant due to low specific activity.

Table 3

Comparison of Radioactivity of Natural Uranium and Irradiated Uranium Purified by the Hermex Process

Material	Gross γ c/min/g U	Gross β c/min/g U	% Difference between Hermex U and Natural U	
			γ	β
Natural U	7.7×10^{4}	8.4×10^{4}		
Hermex-Run 3	4.0×10^{5}	5.6×10^{4}	+500	-30%
Hermex-Run 4	1.7×10^{5}	6.5×10^{4}	+220	-20%

Table 4

Fission Product Distribution in the Hermex Process

Run No	Activity	% of Total Activity						
		Dissolver Slag	Filtered Mercury	Aqueous Wash	Distilled Mercury	Crucible Slag	Product U	Total
3	Gross γ	87	.3	7.9	.007	.26	1.07	97
	Gross β	85	.2	7.8	.0007	1.1	.18	94
4	Gross γ	86	.01	5.8	.2	1.3	.43	94
	Gross β	76	.07	6.6	.3	3.0	.17	86

Table 5

Distribution of β Activity in Irradiated Uranium and the Acid Wash Solution

Activity	% of Total β Activity per Sample	
	Initial Irradiated uranium	Acid Wash Solution
Sr β	26	25
Cs β	32	31
TRE β	42	43
Ru β	0.1	0.2

X-816

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This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

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Mr. S. A. Lawroski, of Argonne National Laboratory, raised the question of the cost of mercury holdup and replacement in the Hermex process. He thought a low limiting concentration of <1 wt % uranium in mercury would make the cost of mercury inventory prohibitive. This seemed to be an important consideration, therefore I determined the cost per pound of uranium for mercury inventory and annual mercury process loss. Certain assumptions were made for fuel geometry in order to calculate dissolving surface available. Dissolution to 0.5 wt % U was assumed to take advantage of the fast initial rate (straight line portion of dissolving curve). The ratio of mercury to uranium in the dissolver was calculated from the rate equation to determine whether or not the geometry of the dissolver would be reasonable.

The calculations follow:

Hermex Dissolver Design Information

A. Assumptions Made in the Hermex Process

1. Continuous processing through washing and drying.
2. Dissolution to 0.5 wt % uranium.
3. No mercury holdup on hot filter.
4. Diameter of declad fuel elements, 0.15 in.
5. Ten percent of the mercury inventory per year will be lost in process.
6. The mercury inventory is three times holdup.
7. Interest charges, 4% per annum.

B. Hermex Dissolver Design

Fuel, declad uranium rods 0.15 in. dia.
Cross section of rods, $cm^2 = (0.15 \times 2.54)^2 \left(\frac{\pi}{4}\right) = 0.114\ cm^2$.
Density of U = $18.7\ g/cm^3$.
Weight of rod per cm length = (0.114)(18.7) = 2.13 g.
Length of rod per pound U = 453.6/2.13 = 213 cm.

Approximate surface of 1 pound of rods (not counting ends) = (3.1416)(0.381)(213) = 255 cm^2/lb U.

The optimum time holdup in the dissolver is 30 min. To determine whether or not the dissolver pot would have a reasonable geometry with this holdup, use is made of the dissolution rate equation, $dC/dt = ks/m(C_s - C)$, where C is the molal concentration of U in Hg at time t; C_s is the molal concentration at saturation (0.047 m); k is the specific rate constant, g·Hg/cm^2/min; s is the U surface, cm^2; m is the mass of mercury used in the dissolution, g; and t is the time, min. Integrated between C = 0 at t = 0 and C_s, it becomes $\log (1 - \frac{C}{C}) = \frac{-ks}{m} t$. At 0.5 wt % U in Hg C is 0.021 m; k = 2.2 g Hg/cm^2 U/min; t = 30 min; C/C_s = 0.448; $1 - C/C_s = 0.552$. Solving, s/m = 0.009 cm^2 U/g Hg. For the U shapes assumed the mercury to uranium mass ratio in the dissolver is 255 cm^2/lb U/0.009 = 24,800 g = 62.5 lb Hg/lb U.

The uranium which will be dissolved by 62.5 lb Hg in 30 min at 0.5 wt % U is 142 g. The mercury required to dissolve 1 lb U in such a dissolver is 200 lb, and the dissolver uranium heel, 3.2 lb/lb U/hr. The mercury feed rate would be 200 lb/hr.

The flowsheet and mercury holdup analysis is shown in Fig. 1.

C. Calculation of Mercury Holdup Per Pound Uranium

From the flowsheet (Fig. 1)

200 lb Hg/lb U/hr for 3/4 hr = 150 lb Hg/hr.
33 lb Hg/lb U/hr for 1 1/4 hr = 41 lb Hg/hr.
Average Hg holdup/lb U/hr = 191 lb
Mercury inventory (3 x holdup) = 573 lb Hg/lb U/hr.
Mercury investment ($3/lb Hg) = $1720/lb U/hr.
Interest for 1 hr at 4% per annum = 1720 x .04/6000 hr/yr = 1.15¢/lb U.
Mercury losses (10% of inventory)/yr = 573 x .10 = 57.3 lb Hg/lb U/hr/yr.

Replacement cost = 57.3 x 3/6000 = 2.87¢/lb U.

Total mercury cost = 2.87 + 1.15 = 4.0¢/lb U.

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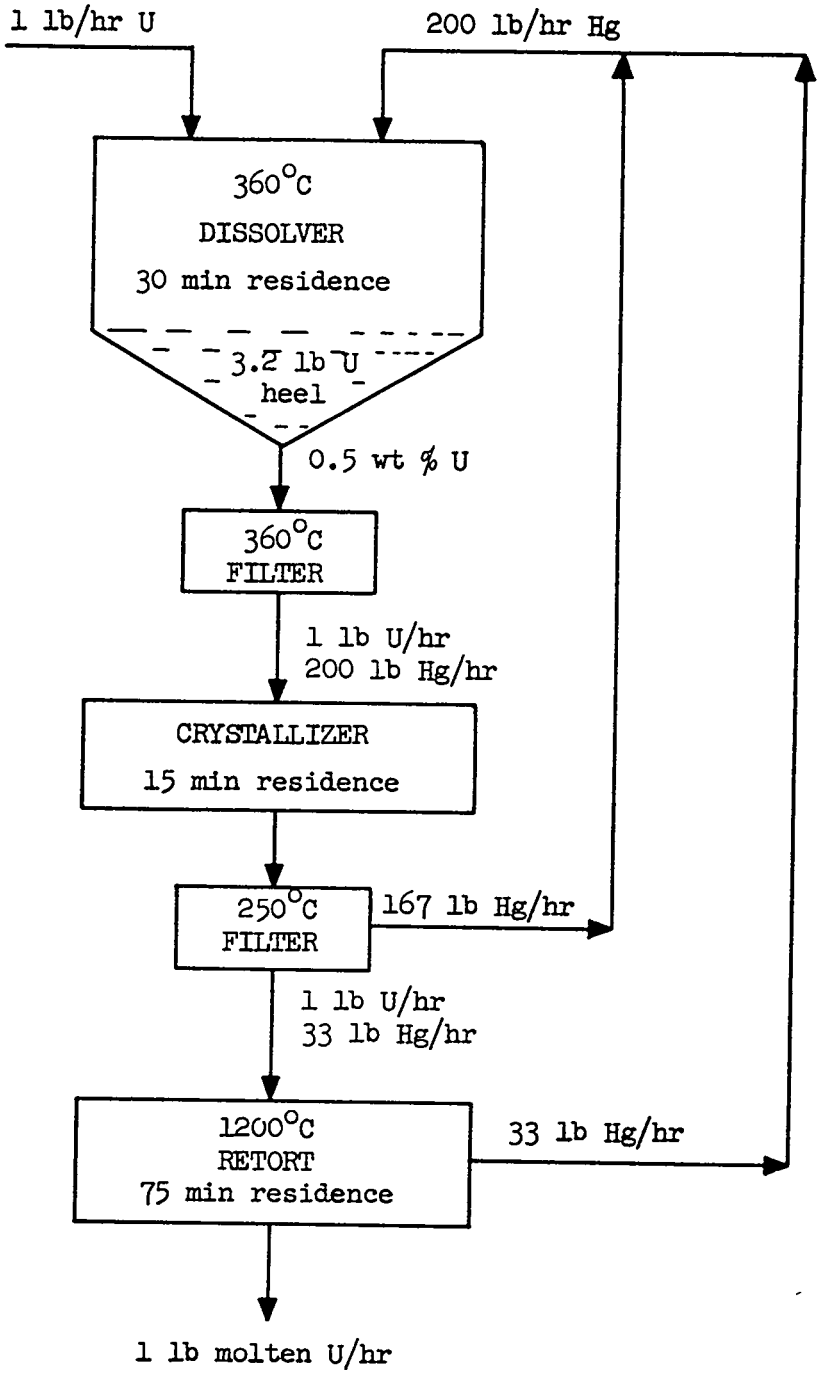

Fig. 1. HERMEX FLOWSHEET AND MERCURY HOLDUP ANALYSIS

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HERMEX PROCESS: THE SOLUBILITIES OF SELECTED METALS IN MERCURY

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For presentation at the ANS Meeting, San Francisco, December 12, 1960

and for review by Nuclear Science and Engineering.

24 pages

4 tables

4 figures

THE SOLUBILITIES OF METALS IN MERCURY

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ABSTRACT

The solubility of uranium and thorium in mercury at 40-356°C ranged from 0.005 to 0.996 atom percent and 0.0019 to 0.0249 atom percent, respectively. For samarium, neodymium, and gadolinium, over the same range of temperature, the solubility was 0.075-0.811, 0.012-0.878, and 0.011-1.05 atom percent. Using equations of the form, $\log N = a + b/T$, heats of solution in mercury were calculated as 6.49 kcal/mole for uranium and 2.93 kcal/mole for thorium; while for samarium, neodymium, and gadolinium they were 4.74, 5.36, and 5.59 kcal/mole, respectively. Uranium solubility in mercury increased in the presence of magnesium, decreased in the presence of thorium, and was unchanged by the presence of ruthenium and palladium. Conversely, the presence of uranium decreased thorium and palladium solubility in mercury but increased the solubility of ruthenium and molybdenum. Trace concentrations of noble fission products from low level irradiations of uranium can be removed with decontamination factors of 5 for each mercury extraction cycle. Higher concentrations, present in "fissiums," can be reduced because of their low solubility in mercury relative to uranium at 356°C.

INTRODUCTION

In the Hermex process (1,2), uranium is purified by dissolution in boiling mercury at one atmosphere, recrystallization of UHg_4 at 25°C, volatilization of mercury at 500°C, and melting. Plutonium has also been purified by analogous methods (3). The basis for separation of impurity metals from these actinides in the dissolution and recrystallization steps is their relative solubilities in mercury at 356 and 25°C.

The purpose of this investigation was to assemble mercury solubility data for metals pertinent to the Hermex process, and where available data were incomplete or suspected to be in error, provide it experimentally.

The solubilities in mercury of uranium, thorium, gadolinium, samarium, and neodymium were determined from 25 to 356°C. The effects of added solutes on the solubilities of uranium, thorium, and some of the major fission products were determined. A table of mercury solubilities of metals (likely impurities and construction metals) pertinent to the Hermex process was computed from published references.

SOLUBILITY DATA AND DISCUSSION

Solubility of Actinides in Mercury

The solubilities in mercury at 40 to 356°C were determined to be from 0.005 to 0.996 atom percent for uranium and 0.0019 to 0.0249 atom percent for thorium, and the logarithms of atomic fractions solubility (log N) were plotted against the reciprocal temperature (Fig. 1). From a least squares fit of data the following solubility equations were derived:

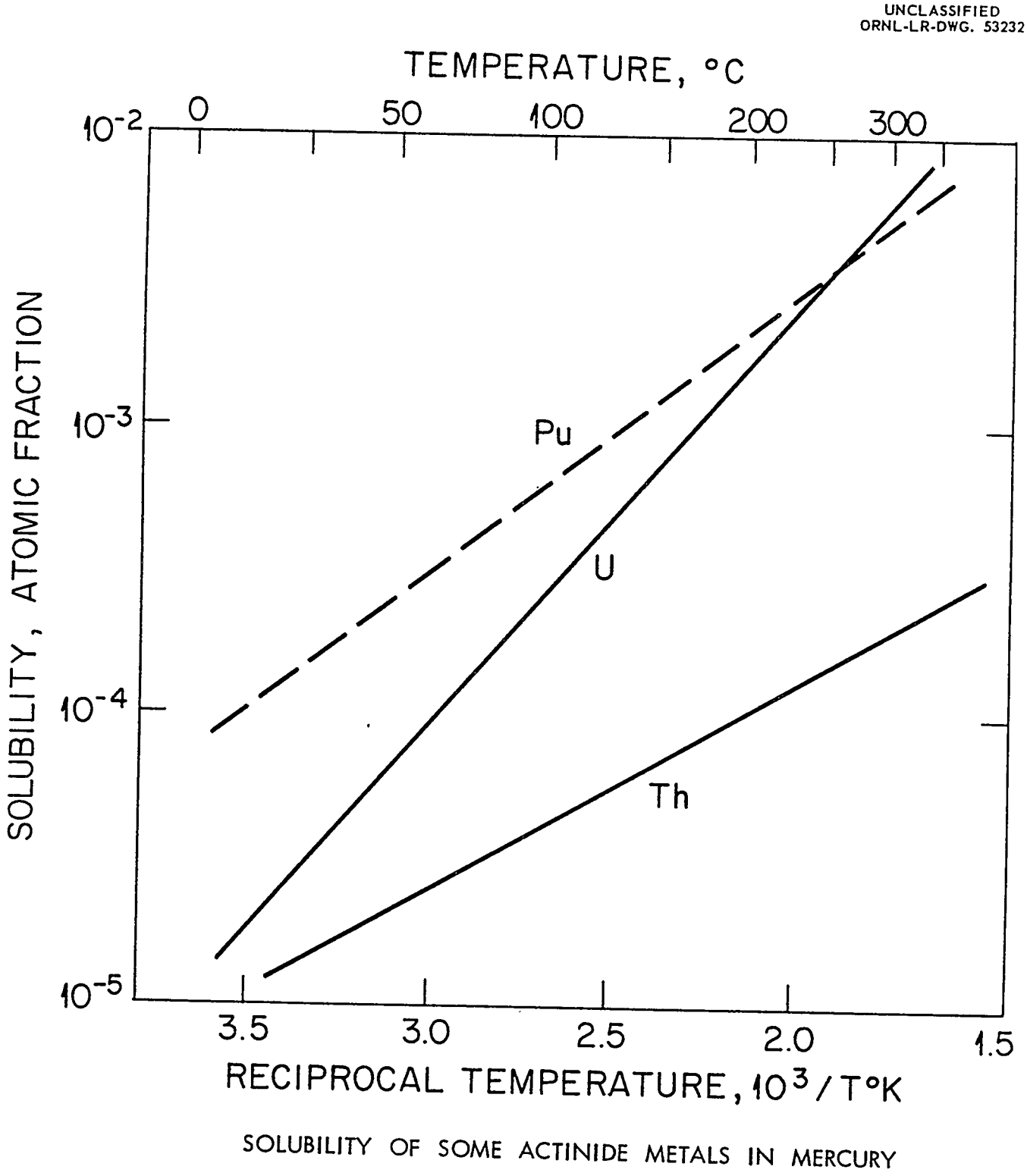

Fig. 1. Solubility of some actinide metals in mercury. Plutonium plot from data of Bowersox and Leary (4).

$$\log N_U = 0.25699 - 1418.81/T \quad (1)$$

$$\log N_{Th} = -2.49394 - 698.47/T \quad (2)$$

with standard errors of fit on logarithms of solubilities of 0.01536 and 0.02046 for uranium and thorium, respectively. From the slopes of the straight line plots and the relationship,

$$\Delta H_S = \frac{R \ln N_2/N_1}{1/T_1 - 1/T_2} \quad (3)$$

the heats of solution were calculated to be 6.49 kcal/mole for uranium and 2.93 kcal/mole for thorium. From the data of Bowersox and Leary (4), the curve for the solubility of plutonium was plotted in Fig. 1 for comparison and reference.

Solubility of Lanthanides in Mercury

Three rare earth representatives, gadolinium, samarium, and neodymium were selected for solubility determinations because of their high fission yield and their significantly high thermal neutron capture cross section (5). Because of the varying degree of completeness in the 4f subshell, each metal represents a sub-class within the rare earth series. Mercury solubilities from 40 to 356°C were 0.011 to 1.05 atom percent for gadolinium, 0.012 to 0.878 for neodymium, and 0.075 to 0.811 for samarium.

Application of least squares to the observed solubility data for the three metals gave the corrected solubilities as a function of reciprocal temperature (Fig. 2), and the following solubility equations and standard errors of fit applied to the logarithms of solubility:

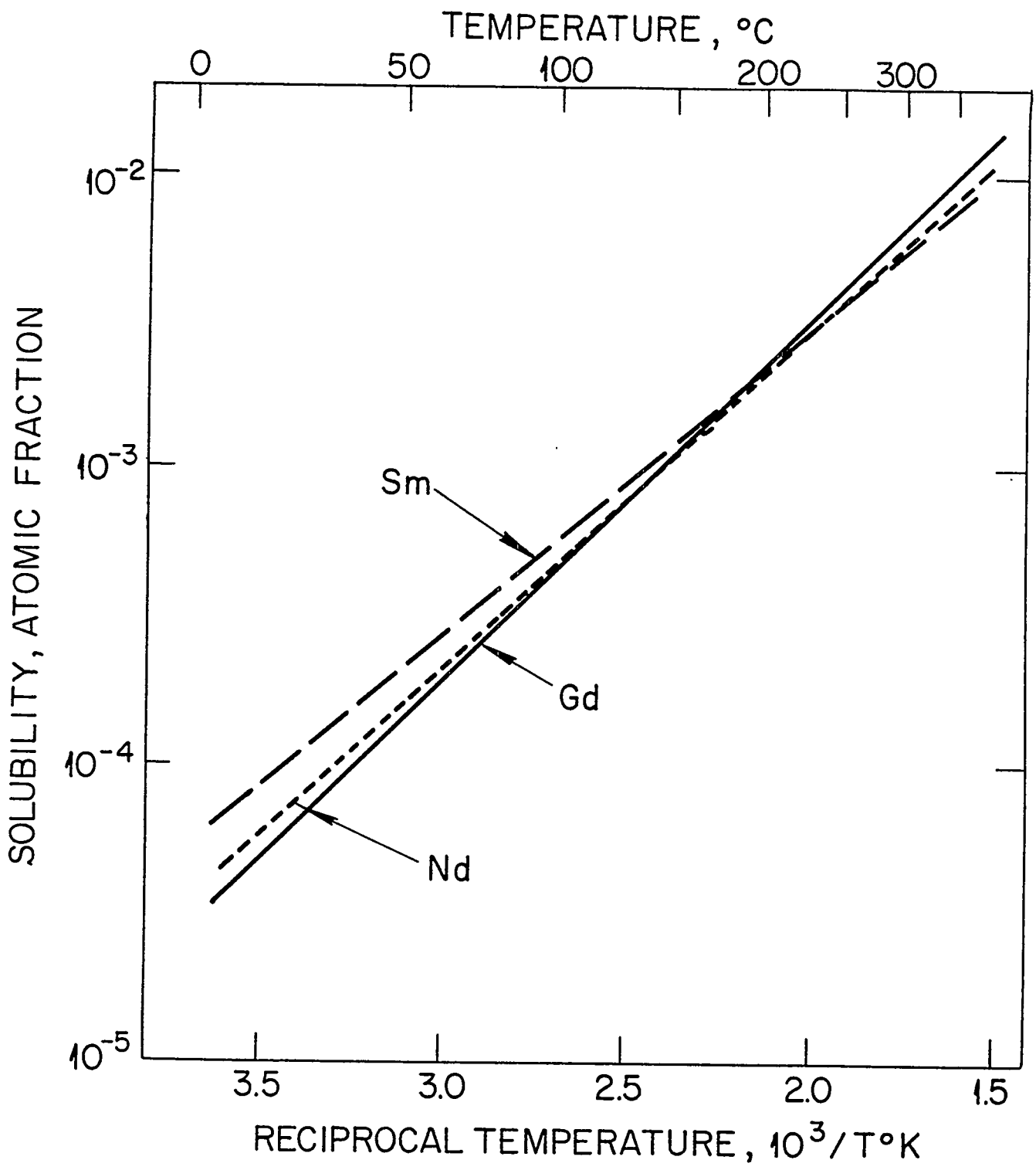

Fig. 2. Solubility of some rare earth metals in mercury.

$$\log N_{Gd} = -0.03632 - 1222.01/T, \quad \sigma_{fit} = 0.03539 \qquad (4)$$

$$\log N_{Sm} = -0.44340 - 1036.45/T, \quad \sigma_{fit} = 0.07606 \qquad (5)$$

$$\log N_{Nd} = -0.20739 - 1163.16/T, \quad \sigma_{fit} = 0.1063 \qquad (6)$$

Calculated molar heats of solution are 5.590 kcal/mole for gadolinium, 4.740 kcal/mole for samarium, and 5.360 kcal/mole for neodymium.

Solubilities of Other Metals in Mercury

The solubilities in mercury of many of the metals of interest to the Hermex process either because they occur as fission products or are used in process equipment have been determined by other workers and are listed in Table I. In some cases, disagreement between references occurs, particularly for the sparingly soluble transition metals. Strachan and Harris (10) report a solubility for ruthenium of 0.353 wt % at 25°C while Leary (3) places it at 1.5×10^{-5} wt % at 350°C and Dean (8) determined it to be 1.7×10^{-7} wt % at 25°C. An estimate from application of the Hildebrand rule (11,12) favors the lower values. Error in determination may arise because these metal solutes are disintegrated by boiling mercury to colloidal particles which are wetted by mercury and are difficult to separate from the mercury solution by filtration or by settling. Where gross disagreement occurred, the Hildebrand rule was used in selecting a preferred value.

It can be seen from Table I that iron, iron-nickel alloys, tantalum, and molybdenum can be used for process equipment without excessive corrosion of structural metal or contamination of the solvent.

Table I. Solubilities in Mercury of Other Elements of Importance to Purification of Uranium

Element	Temperature Range, °C	Solubility Range, wt %	Reference
Cesium	26 - 208	2.98 - completely miscible	6
Strontium	0 - 65	0.75 - 1.79	6
Barium	0 - 95	0.15 - 1.28	6
Cerium	20 - 250	9.6×10^{-3} - 0.547	3
Lanthanum	20 - 250	2.3×10^{-2} - 0.27	3
Manganese	25	1.7×10^{-3}	6
Cobalt	25	8×10^{-5}	7
Antimony	18	2.9×10^{-5}	6
Iron	25 - 350	1.5×10^{-6} - 1.5×10^{-5}	3,6,9
Zirconium	25 - 350	3.3×10^{-6} - 6.9×10^{-4}	3,6
Nickel	25	2×10^{-6}	6
Ruthenium	20 - 350	1.7×10^{-7} - 1.5×10^{-5}	8,3
Molybdenum	350	$<7.4 \times 10^{-6}$	3,7
Niobium	350	$<7.4 \times 10^{-6}$	3
Tantalum	350	$<7.4 \times 10^{-6}$	3

Effects of Added Solutes on Mercury Solubilities

Uranium is 50% more soluble in 0.82 atom percent magnesium amalgam than in mercury at 50°C, and 20% more soluble at 356°C (Fig. 3). In a saturated thorium amalgam, uranium is 20% more soluble at 356°C than in mercury but only one-fourth as soluble at 50°C. Although uranium is about 100 times as soluble as thorium at 356°C in amalgams where both are present to saturation, within experimental error they have approximately the same solubilities at 50°C (Figs. 3 and 4) and this amounts to approximately the solubility of thorium in mercury alone (Fig. 1). This tendency for uranium and thorium to coprecipitate makes the use of the system for separation of the two metals unattractive.

In one experiment, 50 g of an alloy containing 4500 g of uranium per metric ton of thorium was disintegrated in 200 ml of boiling mercury. After filtering the amalgam at 356°C, cooling to 25°C, and refiltering, the product had a U/Th ratio of 0.027. The concentration factor was only 6 where 800 might be expected on the basis of individual mercury solubilities. Less than 20% of the uranium was extracted from the thorium by the hot mercury even though the amount of mercury used was 100 times the requirement for dissolution of all of the uranium present.

By dissolution of 100 g of a uranium-7% "fissium" alloy (defined in Table II) in 200 ml of hot mercury, the solubilities of some of the noble fission products in saturated uranium solution was studied. The alloy contained 2.5% ruthenium, 0.26% palladium, 0.36% zirconium,

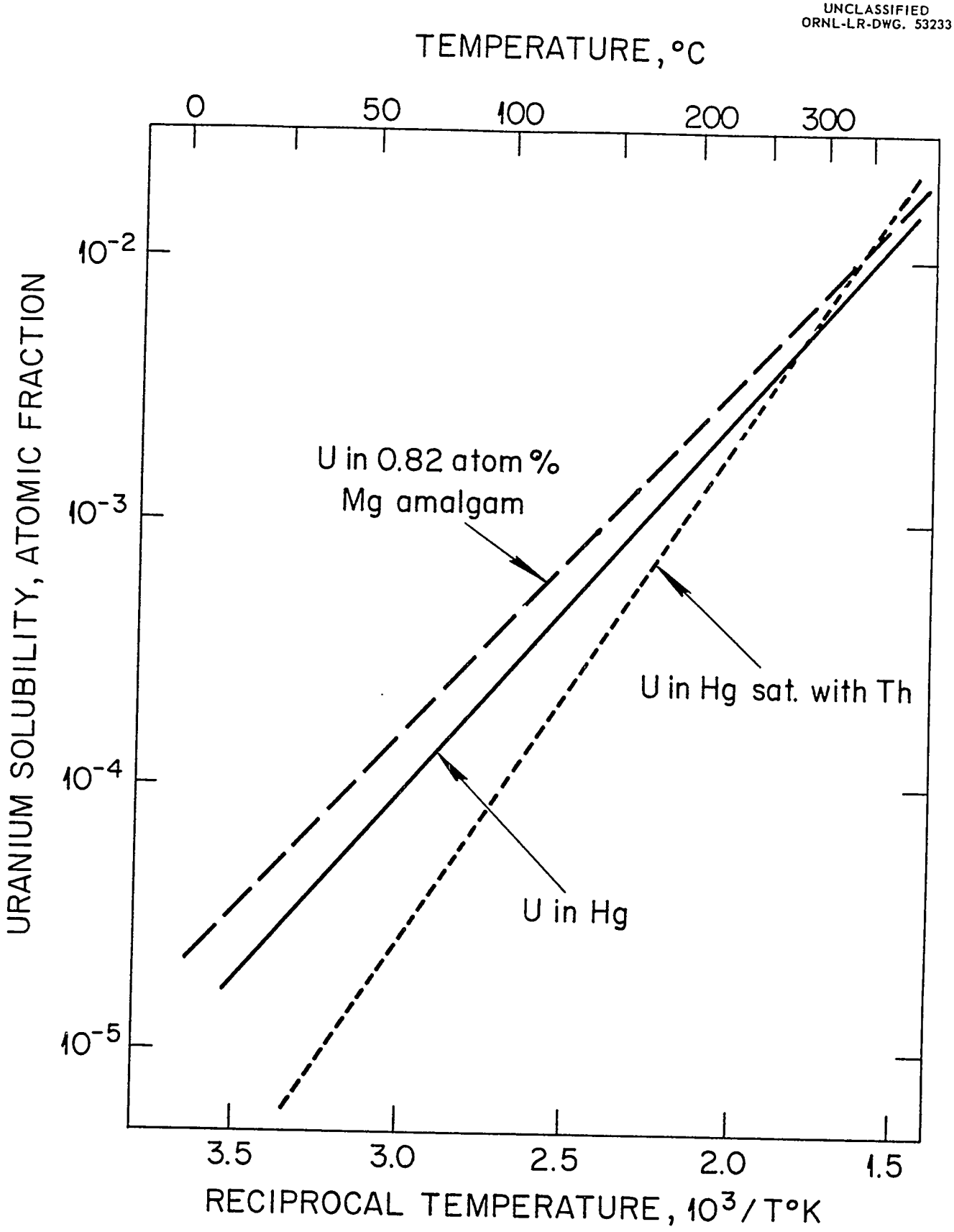

Fig. 3. Effect of added solutes on uranium solubility in mercury.

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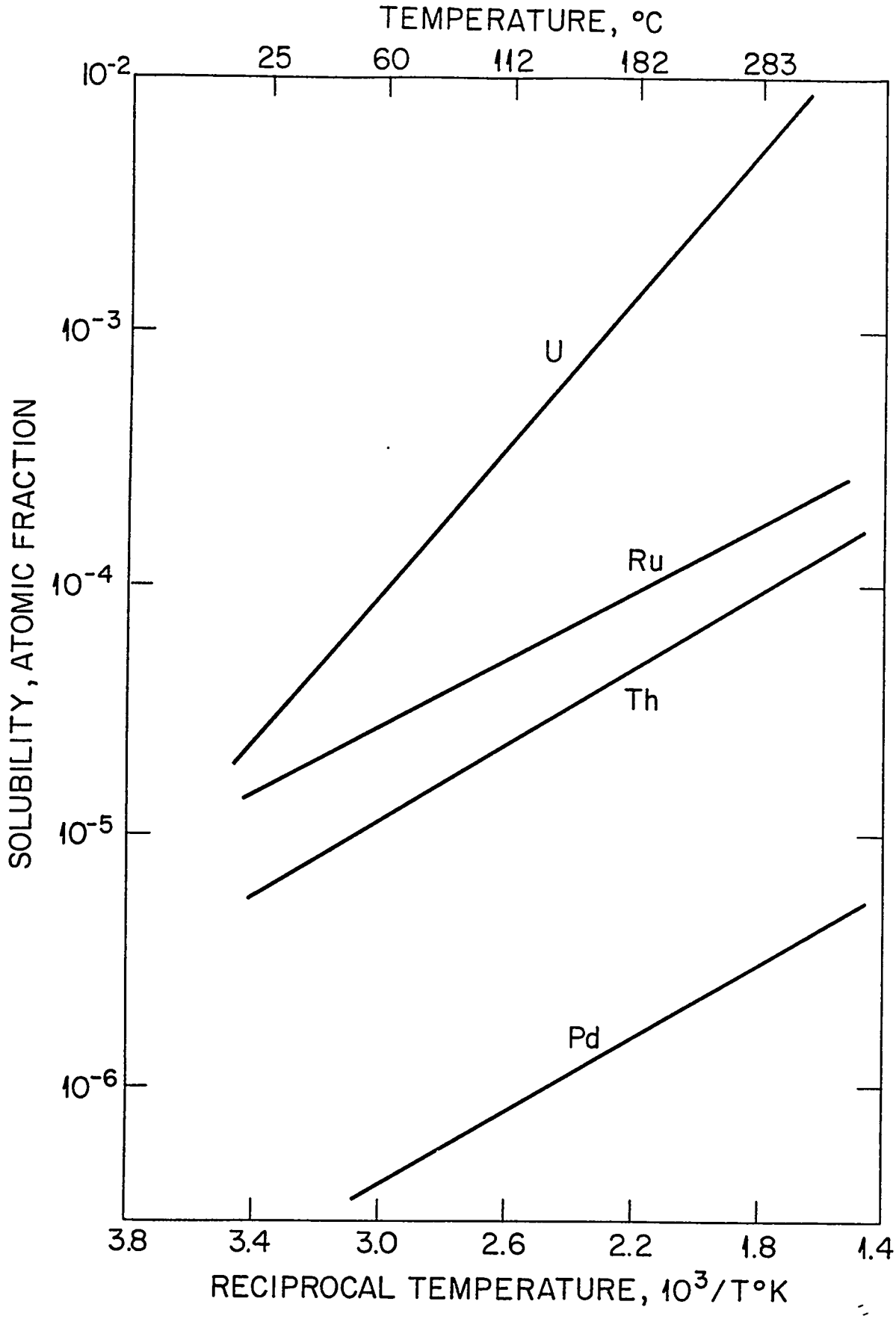

Fig. 4. Solubility of metals in saturated uranium amalgam.

Table II. Comparison of Solubilities at 350°C of Some Metals in Mercury and in Saturated 7% Fissium Amalgam[a]

Metal	Solubility, atom %	
	In Mercury	In Saturated 7% Fissium Amalgam
Ruthenium	1.5×10^{-5}	2.4×10^{-2}
Palladium	1.13×10^{-2}	4.0×10^{-4}
Zirconium	6.9×10^{-4}	4.4×10^{-4}
Molybdenum	1.55×10^{-5}	1.3×10^{-4}
Thorium	2.04×10^{-2}	1.0×10^{-2}
Uranium	1.04	1.0

[a] 7% fissium (13) is a synthetic uranium alloy in which the noble fission product components comprise 7% of the weight of the alloy. The fission product concentrations represent calculated equilibrium values reached when a small side stream (i.e., 5%) of melted metal is withdrawn from a melt refining purification in which uranium is alternately irradiated and melt-refined through about 20 cycles.

0.47% rhodium, 3.35% molybdenum, 0.30% cerium, and the balance, uranium. The entire alloy was disintegrated, and from 2 to 35 wt % of the components were dissolved by the boiling mercury. Sampling during cooling and reheating and analysis by neutron activation gave the curves shown in Fig. 4 for ruthenium and palladium. The curves for the solubilities of thorium in a saturated uranium solution and for uranium in 7% fissium are also shown for reference. The concentrations of molybdenum and zirconium, except at the boiling point of the amalgam, were below the limits of detection in the system by neutron activation and thus could not be plotted. A separate determination of the ruthenium solubility in saturated uranium solution was made using 2% ruthenium-uranium alloy. Solubilities of ruthenium from the fissium and ruthenium alloys agreed within 1%.

In Table II the solubilities of five metals in mercury and in saturated 7% fissium amalgam at 350°C are compared. Since uranium was fifty times as soluble as any other component, its effect on the solubilities of the other components was expected to be more important than their effect on the solubility of uranium. The solubilities of ruthenium and molybdenum were increased 500- and 8-fold by saturation of the mercury with uranium. Zirconium solubility was not significantly affected, but palladium and thorium solubilities were reduced by factors of 300 and 2. The solubility of uranium appeared to be unaffected by the presence of the other fissium components.

Table III illustrates the use of fission product solubilities in mercury and in mercury saturated with uranium to evaluate possible

Table III. Comparison of Expected Decontamination Factors from Fission Products in 7% Fissium in Processing with Mercury, Using Solubilities in Mercury vs Solubilities in Saturated Uranium Amalgam

Basis: 100 g atoms or 20,060 g Hg; sufficient 7% fissium to saturate mercury with uranium (266 g). Uranium dissolved, 247.5 g.

Impurity and Initial Percentage in Alloy	Expected Decontamination Factors	
	Based on Solubility in Mercury	Based on Solubility in Saturated Uranium Amalgam
Ruthenium (2.5)	1940.0	2.9
Palladium (0.26)	1.3	15.7
Zirconium (0.36)	7.0	15.0
Molybdenum (3.35)	6750.0	990.0

decontamination of uranium from four of the fission products in 7% fissium by a single dissolution in boiling mercury followed by crystallization at 25°C. The removal of ruthenium and molybdenum is, in practice, significantly less than one might predict on the basis of individual solubilities.

Removal of Trace Activities from Irradiated Uranium

In experiments reported by Blanco (1) and Dean (2), 30 g of natural uranium irradiated to 1-10 Mwd/ton and decayed 18 days was dissolved in ~300 ml of boiling mercury, filtered under argon at 350°C to remove insoluble fission products, cooled to 25°C to crystallize UHg_4, and then filtered. Residual and chemically bound mercury was separated from the uranium by vacuum distillation at 500°C. The spongy uranium residue was melted at ~1200°C to produce dense purified uranium and slag. Typical decontamination factors obtained from single mercury extractions of these samples were 2-6 for ruthenium, 5 for zirconium, 4-6 for niobium, and 3-4 for plutonium. Reexamination of these results, using the solubility data now available, shows that the concentrations of fission products in these experiments (Table IV) were much less than that required to saturate the mercury system at 25°C, i.e., 7.6×10^{-6} g Ru/g Hg and 1×10^{-2} g Sr/g Hg are mutually soluble with 2.1×10^{-5} g U/g Hg, whereas only 3.2×10^{-9} to 2.6×10^{-8} g Ru or Sr/g Hg are available from the sample. Hence the separation from these fission products was affected mainly in the cold filtration step and was limited by the ratio of mercury in the filtrate to that retained on the filter with the UHg_4 crystals, i.e., 4 to 1.

Table IV. Calculated Decontamination of Uranium Irradiated to Various Levels

Basis: 100 g of irradiated uranium, decayed 18 days

Process: Dissolved in sufficient boiling mercury to produce a saturated uranium solution.[a] Filtered at 350°C to remove insoluble fission products. Cooled to 25°C to crystallize UHg_4. Filtered at 25°C to separate filtrate containing fission products from UHg_4; ratio of filtrate to filter residue, 4/1. Solubilities of U and Ru from Fig. 4.

Original Irradiated Material	Initial Ru Concentration (g/100 g U (5))	Ru Conc. in Product[c] (g/100 g U)	Decontamination Factor		
			Calculated		Experimental
			One Extraction	Two Extractions	One Extraction
Normal U, 1-10 Mwd/T	2.5×10^{-5} to 2×10^{-4}	5×10^{-6} to 4×10^{-5}	5	25	2-6 (2)
Normal U, 3000 Mwd/T	2.2×10^{-2}	4.4×10^{-3}	5	25	-
Fissium (13),[b] 5% dragout from melt refining	2.6	0.923	2.81	3	-

[a] Forty gram atoms of mercury required, of which 38.3 gram atoms is free for dissolution of Ru, and 1.68 is chemically bound by uranium.

[b] Based on 2% of total atoms fissioned with fast fission yields.

[c] The product is the UHg_4 produced by dissolution of the irradiated uranium at 356°C, filtration at 350°C, cooling to 25°C, and filtration at 25°C.

The use of solubilities of noble metal fission products in saturated uranium amalgam (Fig. 4), as well as the versatility of liquid metal solvents for processing uranium, is illustrated in Table IV. The expected decontamination factors from ruthenium of uranium irradiated to various levels and decayed for short times are calculated and, in one case, compared with experimental values. Single irradiations of uranium up to 3000 Mwd/T produce ruthenium concentrations in the uranium below that required to saturate mercury at 25°C when the amount of mercury used is sufficient to dissolve all of the uranium at 356°C. In these cases the amount of ruthenium removed depends on the fraction of free mercury separated by filtration from the UHg_4 crystals at 25°C. Experimentally, 20% of the mercury (and ruthenium) remained with the UHg_4 crystals. Consequently, it should be possible to obtain a high degree of separation by repeated recrystallizations of UHg_4 when the concentration of fission products is low initially.

For low decontamination processes, such as melt refining (13) in which noble metal fission products are not removed with each cycle, the continued buildup in concentration of these products could be controlled by processing a small side stream (i.e., a 5% "dragout") by the Hermex process. In fissium alloys (13), the concentration of noble metals in uranium is such as to provide more than will dissolve in the required mercury at 356°C (see ruthenium, Table IV). Dissolution of the alloy in boiling mercury, followed by filtration at 350°C, would reduce the ruthenium concentration by a factor of nearly 3 because of

its low solubility at 356°C relative to uranium. Crystallization at 25°C and filtration would remove only a small additional increment, due to the relatively low ruthenium solubility in mercury at 25°C. Further redissolutions at 356°C would serve only to redissolve both uranium and ruthenium. Recrystallization at 25°C would also precipitate ruthenium, except for the small fraction dissolved in the mercury filtrate (Table IV). In this case, subsequent mercury extraction cycles would not produce multiples of the first cycle decontamination factor.

Average decontamination factors for cesium of 16 to 130, obtained during the mercury distillation and uranium melting steps, indicated that fission product volatilization is important. Strontium and rare earth activities were retained in dissolution and hot filtration drosses, but mainly in slag from melting (along with ~2% of the uranium) indicating that oxygen was not rigidly excluded. The high decontamination factors for strontium (1000-16,000) and rare earths (600-4700) were attributed to their high reactivities with oxygen.

EXPERIMENTAL

The neodymium, gadolinium, and samarium metals used in this investigation were supplied by the Michigan Chemical Company and were of 99.9+% purity. The 7% fissium alloy was obtained from the Argonne National Laboratory. The 2% ruthenium alloy was prepared by arc-melting the individual metals together and remelting twice. Each of the solubility determinations in this study was made by approaching equilibrium

solubility by heating and by cooling the system containing excess solute to a predetermined temperature. In each case, an inspection of the residue remaining at the conclusion of the run showed that the entire solute sample had been converted to the mercuride. There was only slight evidence of oxidation of the mercurides because of efficient blanketing with purified argon. All except uranium and thorium of the metal solutes formed mercurides which floated, and some of the particles, particularly ruthenium, were colloidal in size. The problem of error due to samples containing undissolved solute particles was lessened by upward withdrawal from the bottom of the dissolver through a heated dip leg containing a "G" Micrometallic filter at its entrance.

APPARATUS

All apparatus used in this study was of stainless steel construction. A 3-in.-dia by 8-in.-deep flanged dissolver was fitted with a cover and sealed with a steel O-ring. The cover had a 1/8-in. argon inlet line, a 1/2-in. water-cooled exhaust line and reflux condenser, a 1/2-in. line with a gate valve for materials addition and sampling, and a thermowell. The top of the gate valve was fitted with a compression seal to prevent in-leakage of air during sampling. An insulated calrod unit served as the heat source.

For sampling, two 3/8-in.-o.d. transfer tubes were used, each of sufficient length to extend from the dissolver bottom, through the inlet gate valve, and to a sample collector. For temperatures of 200°C and below, the tube used had an inside diameter of 1/8 in.,

and for temperatures above 200°C, 3/16 in. Argon or vacuum was supplied to the collector and sample tube during sampling, as required. A stainless steel Micrometallic-G filter with an effective pore diameter of 3 μ was press-fitted into a 3/4-in.-long section of tubing and threaded to the bottom of the transfer tube in use.

PROCEDURE

In a typical experiment 200 ml of triple distilled mercury in the reaction vessel was evacuated, then heated at 150°C under a flow of argon for a 12-hr period to remove gases. The desired quantity of precleaned test material was then introduced against a backflow of argon. In order to assure equilibrium, the test sample was boiled with mercury for several days prior to the first sampling and after each temperature change. Equilibrium solubility for each temperature was approached by cooling saturated solutions from higher temperatures for approximately half of the samples taken and by increasing the temperature of solution in contact with solid mercurides for the remainder.

During the sampling procedure an argon flow through the transfer tube prior to and during its insertion into the dissolver and an increase in the argon flow through the dissolver excluded air. The inserted tube was suspended just above the mercury surface for one-half hour to heat it to the temperature of the amalgam. After the filter tip had been lowered below the surface and the argon flow through the tube discontinued, an additional one-half hour equilibration was allowed. Omission of this step resulted in crystallization of metal mercurides

on and in the filter, plugging it, or preventing transfer of part of the metal solute. To prevent crystallization of the mercurides in the transfer tube during transfer, the section of the tube outside the dissolver was heated by resistance to a temperature somewhat above that of the sample taken. Application of argon pressure to the dissolver and a vacuum to the transfer system forced mercury solution through the filter. With the first appearance of amalgam in the collector, the tube was withdrawn from the mercury solution and that which had passed the filter was forced into the collector.

The 10-20 ml of amalgam collected was dissolved in nitric acid, combined with the internal washings of the transfer tube, and analyzed for the desired components. Samples containing ruthenium and palladium received special treatment because of the insolubility of large fractions of these elements in nitric acid. The insoluble metals were separated from the nitric acid solution by filtration. Ruthenium was separated from palladium by dissolution of the solid residue in 1 M NaOH-1 M NaOCl. Residual palladium was dissolved in aqua regia and added to the alkaline ruthenium solution. Both solutions were then analyzed for each component.

ACKNOWLEDGMENT

The authors are indebted to G. R. Wilson, G. W. Leddicotte, and P. F. Thomason and staffs of the ORNL Analytical Chemistry Division and to H. R. Guinn and staff of the Special Testing Laboratory for analyses performed. Acknowledgment is made to E. R. Johns who performed much of the laboratory work.

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HERMEX PROCESS: THE SOLUBILITIES OF SELECTED METALS IN MERCURY

by

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To be presented at the AES Meeting, San Francisco, December, 1960

O. C. Dean is a member of the American Nuclear Society.

HERMEX PROCESS: THE SOLUBILITIES OF SELECTED METALS IN MERCURY

C. C. Dean* and A. F. Messing**

ABSTRACT

In the Hermex Process[1] uranium is purified by dissolution in boiling mercury, recrystallization of UHg_4 at 25°C, volatilization of mercury under vacuum at 500°C, and melting. Plutonium has also been purified by a similar method.[2] Processes have also been developed for the reduction of uranium and thorium compounds to metals by alkali metal amalgams.[3,4] In the recrystallization method the relative solubility of the metals is the basis for separation. Consequently, the solubilities of pertinent metals in mercury as a function of temperature were tabulated from existing data or were determined when such data were lacking or in doubt.

A plot of the logarithm of atomic fraction solubilities against the reciprocal of absolute temperature by the least square method for uranium, thorium, gadolinium, neodymium, and samarium gave the following equations. The corresponding standard errors of fit are also listed:

$$\log N_U = 0.25699 - 1418.81/T;\ \sigma_{fit} = 0.01536;\ \Delta H = 6490 \text{ cal/mole} \quad (1)$$

$$\log N_{Th} = -2.49394 - 698.472/T;\ \sigma_{fit} = 0.02046;\ \Delta H = 2930 \text{ cal/mole} \quad (2)$$

$$\log N_{Gd} = -0.03632 - 1222.01/T;\ \sigma_{fit} = 0.03539;\ \Delta H = 5590 \text{ cal/mole} \quad (3)$$

$$\log N_{Nd} = -0.80739 - 1165.16/T;\ \sigma_{fit} = 0.1063;\ \Delta H = 5360 \text{ cal/mole} \quad (4)$$

$$\log N_{Sm} = -0.44340 - 1036.45/T;\ \sigma_{fit} = 0.07606;\ \Delta H = 4740 \text{ cal/mole} \quad (5)$$

where N is the atomic fraction of the respective solutes, ΔH is the heat of solution of the solute, and T the absolute temperature in degrees Kelvin. The heat of solution was calculated from the relationship

$$\Delta H_s = \frac{R \ln N_2/N_1}{1/T_1 - 1/T_2} \quad . \quad (6)$$

The solubilities of some metals in mercury are affected by the presence of others in the same solution. The solubilities of uranium and thorium were

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mutually decreased when both were present, and the effect was increased as temperature was decreased. This tendency for uranium and thorium to coprecipitate from cooled mercury solutions makes the separation of small concentrations of uranium from thorium by crystallization from mercury unattractive. The solubilities of ruthenium and zirconium in mercury were increased 1000-fold by saturating the solution with uranium (Table I) and

Table I

Comparison of Solubilities of Metals in Mercury and in Mercury Saturated with Uranium at 25 to 350°C

Element	Solubility in Mercury, wt %		Solubility in Mercury Saturated with Uranium, wt %	
	25°C	350°C	25°C	350°C
Thorium	0.015	0.0235	0.0007	0.0118
Ruthenium	-	1.6×10^{-7}	6×10^{-4}	8×10^{-3}
Zirconium	-	6.8×10^{-6}[a]	5×10^{-5}	2×10^{-4}
Molybdenum	-	7.4×10^{-8}[a]	8×10^{-6}	3×10^{-5}

[a]Known at 300°C only.

both metals coprecipitated with uranium on cooling. In a series of experiments uranium, irradiated to 5×10^{17} nvt, was dissolved in mercury at 350°C and crystallized as UHg_4 at 25°C. The decontamination factors for cesium and plutonium were 130 and 3, as predicted on an individual solubility basis, but ruthenium, zirconium, and niobium factors were lower than predicted, i.e., 6, 5, and 4, respectively, probably due to the effects of uranium on their solubilities. Unexpectedly high decontamination factors for strontium and rare earths ($\sim 10^4$) were attributed to their high reactivity with traces of oxygen and separation as an oxide slag. The concentrations of strontium and rare earths are extremely low at this irradiation level.

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The Hermex process promises to be a cheap method for purification of uranium metal and alloys up to 2% in zirconium. However, at the present stage of development it is not adaptable to alloys of 10% and more of molybdenum or zirconium. It is my understanding that the prime reasons for substituting alloys for pure uranium are: (1) the alloys are more dimensionally stable under conditions of irradiation and thermal cycling; (2) the alloys are more resistant to the attacks of water at high temperatures.

If the objectionable features of uranium could be circumvented by reactor and/or fuel element design, the Hermex processing scheme might show considerable economic advantage over other reprocessing schemes for power reactors.

I should like to propose a fuel element of the following approximate structure. A can, positioned vertically in the reactor is to be filled with small rods, wires, or pellets of uranium, and the voids filled with molten sodium. The ends of the cans should be so equipped that they can be remotely removed without destruction, in order to discharge the contents to a Hermex reprocessing vessel. The fuel element is to be surrounded by another tube, which provides a channel for sodium coolant. A gas space should be provided at the top of each element, connected to a header to serve as a pressure relief and as a bleed for fission product gases (Fig. 1).

It is my belief that a system similar to this could be made simple to unload, reprocess, and reload, and that dimensional stability of U would be unimportant.

Metals having good resistance to reasonably oxygen-free Na or NaK at 300-800°C are pure iron, ferritic stainless steel (25-20, Cr-Ni), austenitic stainless (18-8, Cr-Ni), chromium, cobalt-base alloys, molybdenum, niobium, tantalum, tungsten, nickel alloys with Fe, Cr, or Mo, zirconium or Zircaloy. Of these, the materials of low thermal cross

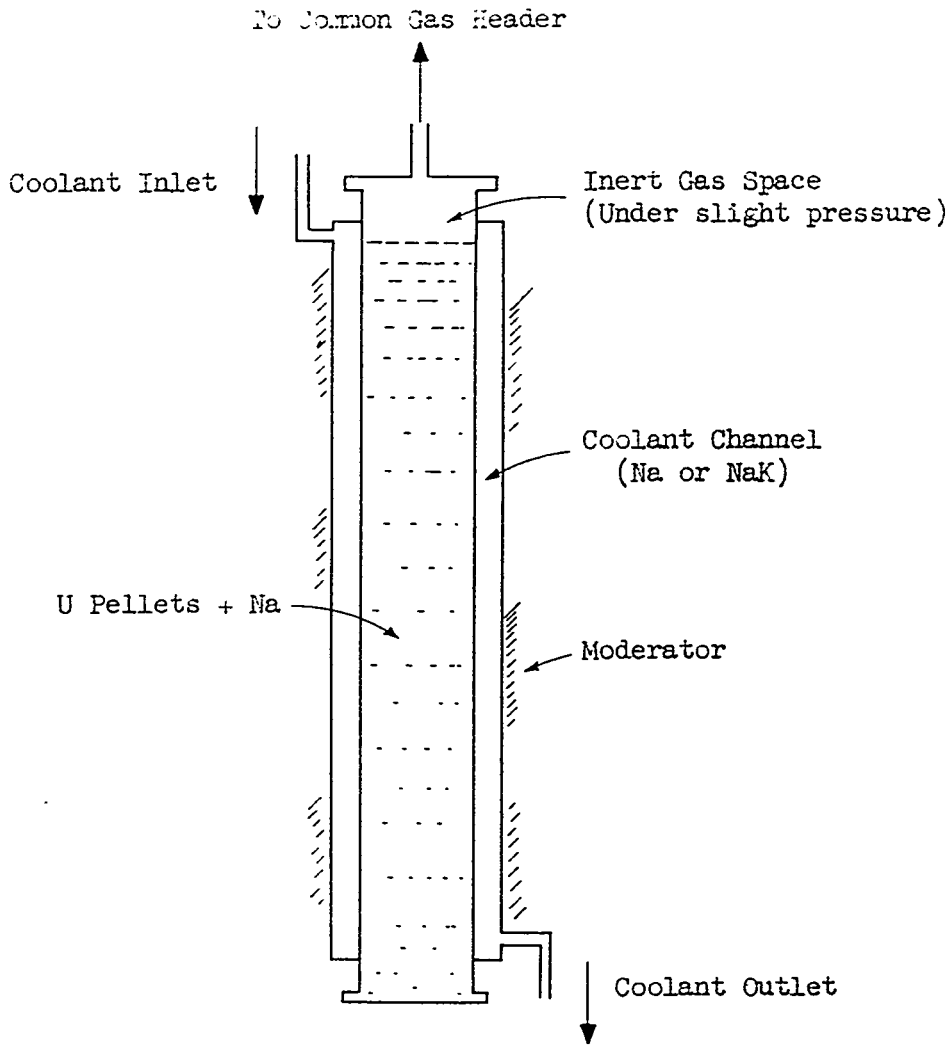

Fig. 1 REACTOR FUEL ELEMENT

section are zirconium, Zircaloy, niobium, and, to a lesser extent, iron and the ferrous alloys.

Sodium does not alloy with uranium, and the solubility of U in Na is of the order of 10 ppm at 350°C. The feasibility of forming U pellets from molten uranium using a rotating disc has been proven in recent experiments at Fernald.

The Hermex reprocessing flowsheet is shown in Fig. 2. Present thinking is to eliminate the amalgam washing step and depend on recrystallization for purification. It is suggested that the Hermex dissolver and the bottom of the reactor element be so engineered that the spent reactor fuel may be directly discharged into the dissolver pot, and the dissolver pot be attached by quick disconnects to the Hermex processing train.

O. C. Dean

OCD/jr

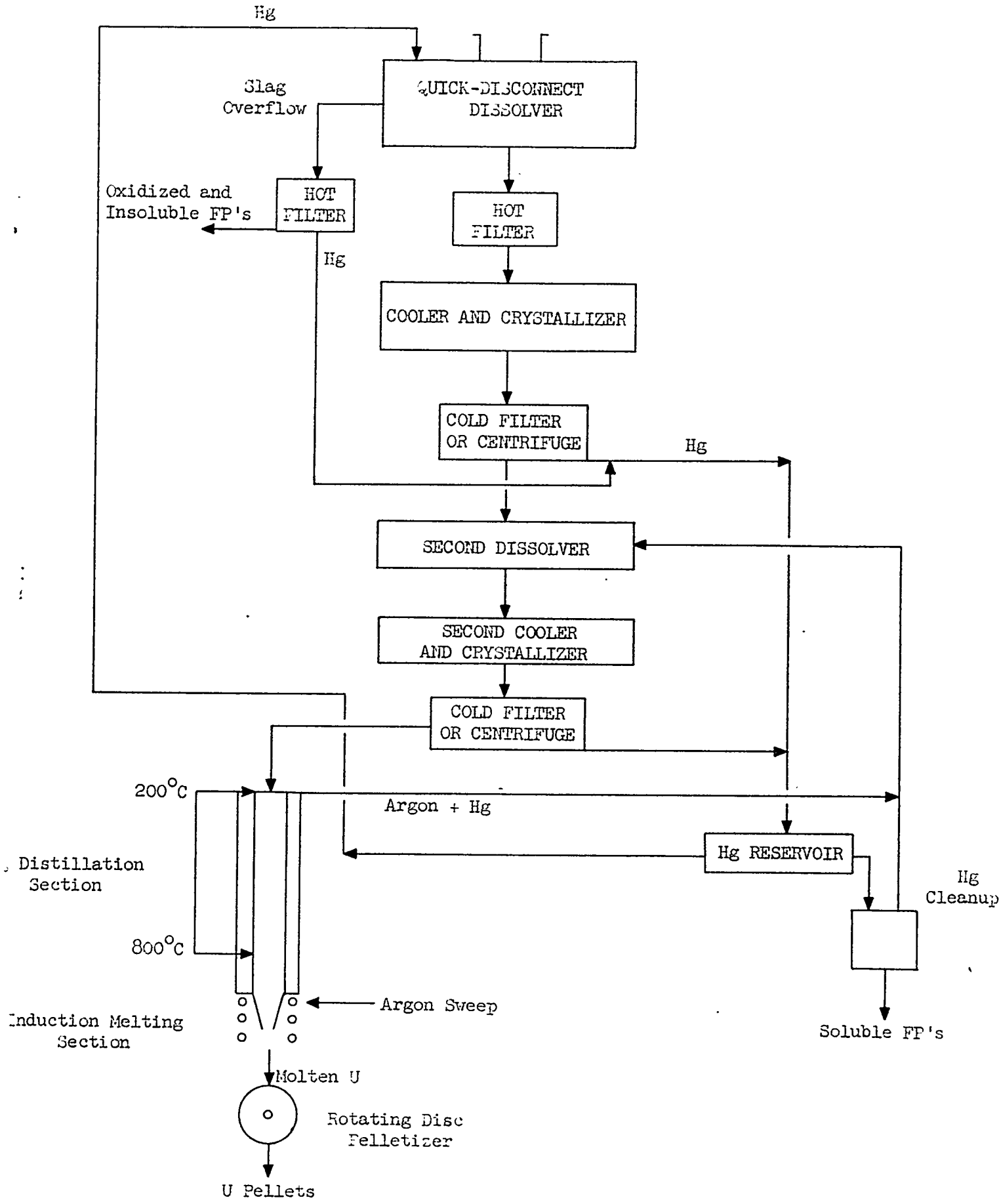

Fig. 2 HERMEX PROCESSING RECRYSTALLIZING SCHEME

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Mercury Assessment for Water and Sediment in Oak Ridge National Laboratory Streams

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ORNL/M-713

MERCURY ASSESSMENT FOR WATER AND SEDIMENT IN OAK RIDGE NATIONAL LABORATORY STREAMS

Fred G. Taylor, Jr.

Environmental and Health Protection Division

Date Published: March 1989

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
operated by
Martin Marietta Energy Systems, Inc.
for the
U. S. Department of Energy
under Contract No. DE-AC05-840R21400

ACKNOWLEDGMENTS

The assistance of B. R. Hensley and D. W. Parsons (Environmental and Health Protection Division) is greatfully acknowledged for sample collection and W. Musick (Analytical Chemistry Division) for providing the analytical chemistry services.

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1.0 INTRODUCTION

An assessment plan was implemented in compliance with the Clean Water Act and the Oak Ridge National Laboratory's (ORNL) National Pollutant Discharge Elimination System (NPDES) permit to identify, locate, and minimize all sources of mercury contamination in ORNL discharges to the aquatic environment. This plan was designed to identify sources of mercury from past operations and spills through a review of file records and personal interviews. A network of monitoring and sampling stations, based on knowledge of mercury deposits in receiving streams, knowledge of mercury discharges from pipes to streams, and a review of chemical data from previous contaminant surveys, was established for sample collection. The plan was designed to assess the potential for the metal reaching surrounding streams and rivers by placement of sampling sites relative to potential contaminant movement from areas of deposition. This summary report describes appropriate sampling and analytical procedures, defines the database management system, provides for chain-of-custody, Quality Assurance (QA), and presents contaminant concentration data for 1988.

2.0 AREA RECEIVING WATERS

Effluents from the numerous laboratories at ORNL are treated and subsequently monitored before discharging into the receiving streams at permissible concentrations. In previous years, before stringent regulations, some contaminants reached various streams primarily as the result of accidental spills and leakages. The intent of this effort is to identify sources or pools of a single heavy metal (mercury) and to characterize the extent and the specific locations of contamination. A summary of area receiving streams or bodies of water is provided with a brief description of potential contaminant sources.

2.1 CLINCH RIVER-MELTON HILL LAKE

This body of water receives discharge from two holding ponds in the Fuel Recycle area. These ponds are categorized as Category I (storm water) and Category II (cooling tower discharge) outfalls.

2.2 CLINCH RIVER-WATTS BAR LAKE

Downstream from Melton Hill Dam, the Clinch River-Watts Bar Lake receives all the wastewater discharge from ORNL with the exception of that from the two holding ponds listed in the above paragraph.

2.3 WHITE OAK CREEK

This perennial stream enters north of the ORNL site from Chestnut Ridge and runs along the main Bethel Valley complex collecting discharges from Category I, II, and III outfalls; miscellaneous source outfalls; and

point source outfalls X01, X02, X04, X06, X07, and X11. Fifth Creek, First Creek, and Northwest Tributary join White Oak Creek in Bethel Valley and Melton Branch joins White Oak Creek in Melton Valley.

2.4 FIFTH CREEK

This small stream originates from springs at the base of Chestnut Ridge and enters the north side of the ORNL main complex in Bethel Valley and receives discharges from Category I, II, and III outfalls. At the south end of the ORNL site Fifth Creek joins White Oak Creek.

2.5 FIRST CREEK

This stream originates from springs near the base of Chestnut Ridge and enters the north side of the ORNL main complex in Bethel Valley where it receives discharges from Category I, II, and III outfalls. First Creek is joined by Northwest Tributary at the south end of the ORNL site and enters White Oak Creek.

2.6 NORTHWEST TRIBUTARY

This stream originates primarily from springs near the base of Haw Ridge and enters the west side of the ORNL complex in Bethel Valley where it receives discharge from the X03 point source outfall. Northwest Tributary joins First Creek before entering White Oak Creek.

2.7 MELTON BRANCH

Several small springs from Haw and Copper Ridges combine to form Melton Branch. Melton Branch enters the east side of Melton Valley where it receives discharges from Category I, II, and III outfalls and point source outfalls X08 and X09. Melton Branch joins White Oak Creek approximately 0.5 km (0.3 mile) above White Oak Lake.

2.8 WHITE OAK LAKE

This impoundment serves as the last monitoring point and holding basin for wastewater discharges leaving ORNL. No outfalls discharge directly into the lake.

3.0 MERCURY SOURCES (SPILLS)

Two major uses of mercury at ORNL involved pilot plant operations in 1954-55 supporting the thermonuclear weapons program at Y-12. Both activities involved separation processes in Buildings 4501 and 4505. At the time of the operations, an unknown number of mercury spills occurred. Although these spills were cleaned up, it is evident from soil analyses around the buildings that quantities of mercury escaped and reached the environment (Oakes, 1983a,b). Key individuals with personal knowledge of the operations were interviewed concerning the history of mercury spills.

A summary is provided of each process with estimates of mercury lost through operational procedures, and included with additional reportable incidents in Table 1.

Table 1. Summary of known mercury spills at ORNL

Building	Process	Year	Amount	Outfall
4501	Lithium isotope separation	1954	>23,000 kg	362,363
4505	Uranium and thorium metal production (Metallex)	1955	2,000 kg	362,363
3592	Mercury cleaning (Orex)	<1963	5,000 kg	207
3503	Mercury flask and clean mercury storage	<1963	unknown	207
2525	Spill	1981	1.5 kg	103,207, 208
4500S	Spill	1980	<1.0 kg	109,217, 218,311
3500	Spill	1981	<0.02 kg	163,162, 261,361, 207

3.1 BUILDING 4505, EXPERIMENTAL ENGINEERING LABORATORY

A process termed METALLEX was demonstrated in 1955 in Building 4505 to illustrate the production of uranium and thorium metals by reducing UCl_4 or $ThCl_4$ using sodium amalgam. The amalgam was pressed to form a billet and the billet was sintered to remove the mercury by vacuum distallation leaving the uranium or thorium metal. An early report indicated as much as 134,608 kg (296,139 lb) of mercury were required as materials for the process. Personnel involved in the project estimate that 2000 kg (4400 lb) may have been lost in spills (Dinsmore, 1986). Soil analyses near the building confirm mercury contamination (Oakes, 1983b).

3.2 BUILDING 4501, HIGH-LEVEL RADIOCHEMICAL LABORATORY

The OREX process was similar to the METALLEX procedure but was designed to separate lithium isotopes. The lithium was amalgamated, pressed into billets, sintered, and the mercury removed by vacuum

distillation leaving the lithium. This process was carried out in the basement of Building 4501 in 1954. The basement floor was of concrete construction with tar seams and was flooded with 10 cm (4 in) of water. The water layer was intended to reduce mercury fumes in the building atmosphere. A steel grate above the water pool supported equipment and personnel. Throughout the process some mercury escaped from the basement at the tar seams as is confirmed by soil analyses (Oakes, 1983b). The condensed mercury was pumped to a tank truck where it was transferred to Building 3592 for cleaning and recycle. It has been estimated that an excess of 22,680 kg (50,000 lb) of mercury may have been lost during the process (Parker, 1986). Most spills were associated with pump failures where amalgam was being pumped from the basement to the upper level of Building 4501.

3.3 BUILDING 3592, UNIT OPERATIONS VOLATILITY LABORATORY

Mercury distilled from the OREX process was transported to Building 3592 for cleaning by resin exchange columns. Following cleaning, it was placed in containers and later removed to Y-12. A spill occurred due to operator error which involved 400 gal (20,500 kg) of mercury. Approximately 300-350 gal were recovered by vacuum sweeping. The remainder, 50-100 gal (2500 to 5000 kg), was lost to the surrounding soil, subject to transport to White Oak Creek through the Laboratory storm drain system (Dinsmore, 1986). Soil and sediment analyses confirm contamination by mercury (Oakes, 1983a).

3.4 BUILDING 3503, HIGH RADIATION CHEMICAL ENGINEERING LABORATORY

Building 3503 was used to store empty mercury flasks and cleaned mercury from the resin columns of Building 3592. By 1963 all the materials associated with METALLEX and OREX had been removed to Y-12. Some small quantity of mercury may have reached White Oak Creek through the Laboratory storm drainage system. No estimate is available of the amount spilled in Building 3503. Analyses of the Building 3503 storage area confirm that mercury had escaped the building (Oakes, 1983a).

3.5 BUILDING 2525, PLANT AND EQUIPMENT FABRICATION SHOP

In May of 1981, mercury was reported in the drain system from Building 2525. The origin of the spill was reported as unknown. Less than 1.5 kg (3 lb) were removed by vacuum cleaning and submitted for cleanup and recycle (Eisenhower, 1981; Kelly and Eisenhower, 1982).

3.6 BUILDING 4500S, CENTRAL RESEARCH COMPLEX

Two minor spills are recorded (Kelly and Eisenhower, 1982) from laboratories in the Central Research Complex (Building 4500S) during 1980. The quantities were noted as a trace (<10 g) and 100 g. One spill was noted as operator error and the other as mechanical failure. In both cases there was no mention of the action taken.

3.7 BUILDING 3500, INSTRUMENTATION AND CONTROLS

An undisclosed quantity of mercury was reported as a spill in 1981. Kelly and Eisenhower (1982) indicated it was a "puddle" (10 to 20 g) and resulted from operator error.

4.0 SAMPLE LOCATIONS

As a means of establishing baseline data for environmental concentrations of mercury, water was collected from receiving streams near the various Laboratory outfalls. Areas sampled included selected Category I, II, and III outfalls; NPDES Serial Numbered Sampling sites; and areas surrounding known mercury spills. Category I outfalls receive water from storm drains. Those outfalls sampled are identified in Table 2 and were selected on the basis of the potential for water transport from areas near buildings with a past history of mercury concern. Category II outfalls (Table 3) include storage area drains, spill area drains, roof and parking lot drains, and cooling tower blowdown and condensate drains. Although the potential for mercury entering these systems is minimal, several outfalls were identified for sampling. Category III outfalls receive routine process wastes and periodic laboratory wastes. These systems represent the greatest potential for mercury transport to receiving streams. Outfalls sampled are identified in Table 4. The Serial Numbered Sampling sites routinely sampled for radiological contaminants (Table 5) are included to provide a broader survey for mercury in the Laboratory's receiving streams.

Table 2. Candidate Category I sampling stations by outfall number and receiving stream

WHITE OAK CREEK	
Outfalls:	101, 103, 106, 109, 116
FIRST CREEK	
Outfalls:	141, 142, 143
FIFTH CREEK	
Outfalls:	161, 162, 163, 164
MELTON BRANCH	
Outfall:	181

Table 3. Candidate Category II sampling stations[a] by outfall number and receiving stream

WHITE OAK CREEK	
Parking Lot Runoff:	202, 204, 207, 208, 210, 218, 222, 223, 230, 232, 233, 234
Condensate:	217
Cooling Tower Blowdown:	216
Spill Area Drain:	206
FIRST CREEK	
Parking Lot Runoff:	241, 243, 247, 248,
Storage Area Drain:	244, 246
MELTON BRANCH	
Parking Lot Runoff:	283
Cooling Tower Blowdown:	281
FIFTH CREEK	
Parking Lot Runoff:	265
Condensate:	261, 262
Cooling Tower Blowdown:	268

[a]Roof drains, parking lot drains, storage area drains, spill area drains, once-through cooling water, cooling tower blowdown and condensate

Table 4. Candidate Category III sampling stations (process or laboratory drains) by outfall number and receiving system

WHITE OAK CREEK	
Process Drains:	301, 302, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314
FIFTH CREEK	
Process Drains:	361, 362, 363, 364, 365, 366, 367, 368
MELTON BRANCH	
Settling Ponds:	381, 382, 384, 385, 386
FIRST CREEK	
Process Drains:	341, 342, 343, 344

Table 5. Candidate serial numbered outfalls (point sources) and receiving streams

White Oak Creek:	X01 - Sewage Treatment Plant, X02 - Coal Yard Runoff, X04 - 2000 Area, X06 - 190 Process Ponds, X07 - Process Waste Treatment, X11 - Acid Neutralization Facility
First Creek:	X12 - NRWTF
Melton Branch:	X08 - TRU, 7907 and 7908 Ponds, X09 - HFIR, 7905 and 7906 Ponds
Northwest Tributary:	X03 - 1500 Area Pit

Several additional sites which are routinely sampled for other contaminants are included in the sampling design. These are White Oak Dam, White Oak Creek, Headwaters of White Oak Creek, Melton Hill Dam, Melton Branch, Headwaters of Melton Branch, 7500 Bridge (White Oak Creek), and the White Oak Creek Flume south of Waste Basins 3539 and 3540.

A total of 90 sites (Table 6) were available for sampling (water) during the survey with an additional 12 sites for sediment samples. Sampling sites in the ORNL Bethel Valley complex are noted in Fig. 1, while sites in the Melton Valley area are illustrated in Fig. 2. In a preliminary survey (1987), 74 sites (222 analyses) were sampled for water analyses, in comparison to 61 sites (183 analyses) in February 1988; 88 sites (264 analyses) were sampled in October 1988. An additional 12 sites (36 analyses) were sampled in October 1988 for mercury contamination of sediments. Most sites were sampled twice during the year and consisted of three replicate samples for each site. The sampling periods were selected to represent periods of soil moisture recharge and soil water deficit. Sediment samples were primarily from Fifth Creek in the vicinity of suspected mercury deposition, White Oak Creek, and White Oak Creek headwaters.

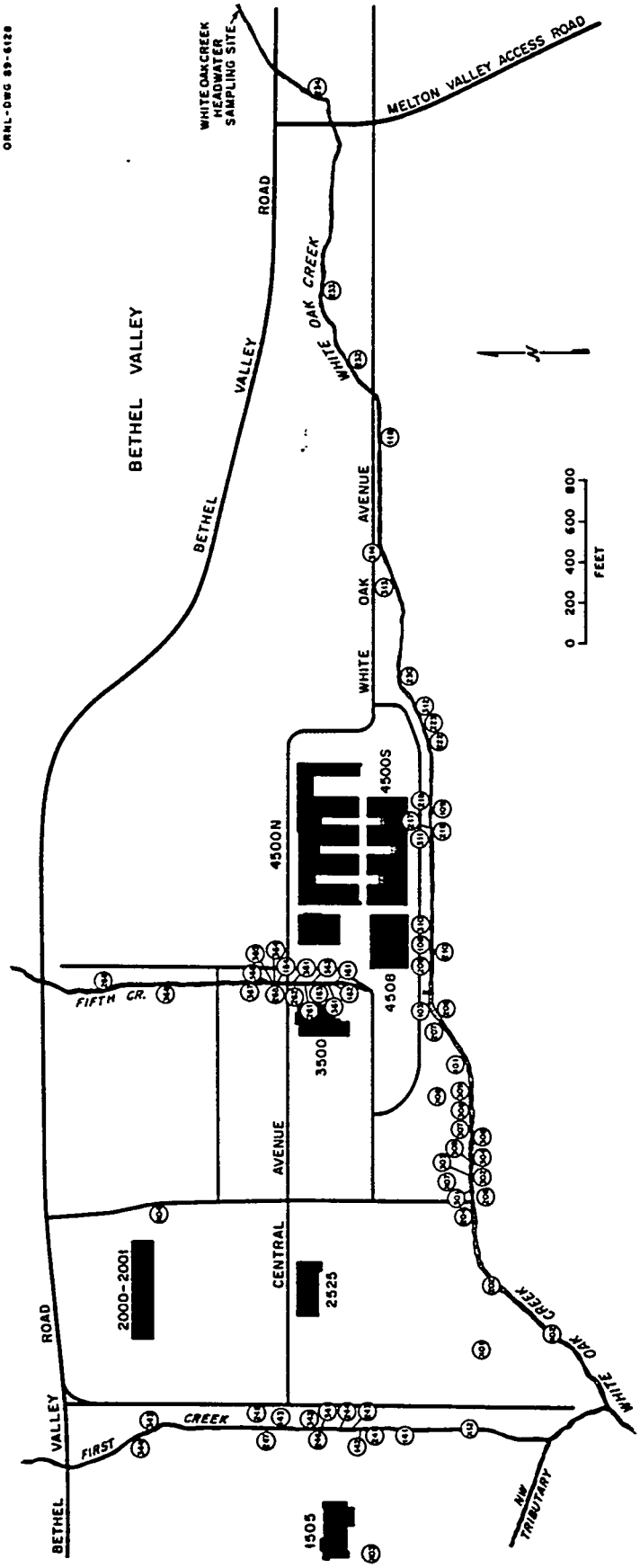

Fig. 1. Sampling stations in the ORNL Bethel Valley complex. The circled numbers are positioned as near as possible to the outfall. Series Number (100, 200, 300, or X) corresponds to the outfall categories identified in Tables 2-6.

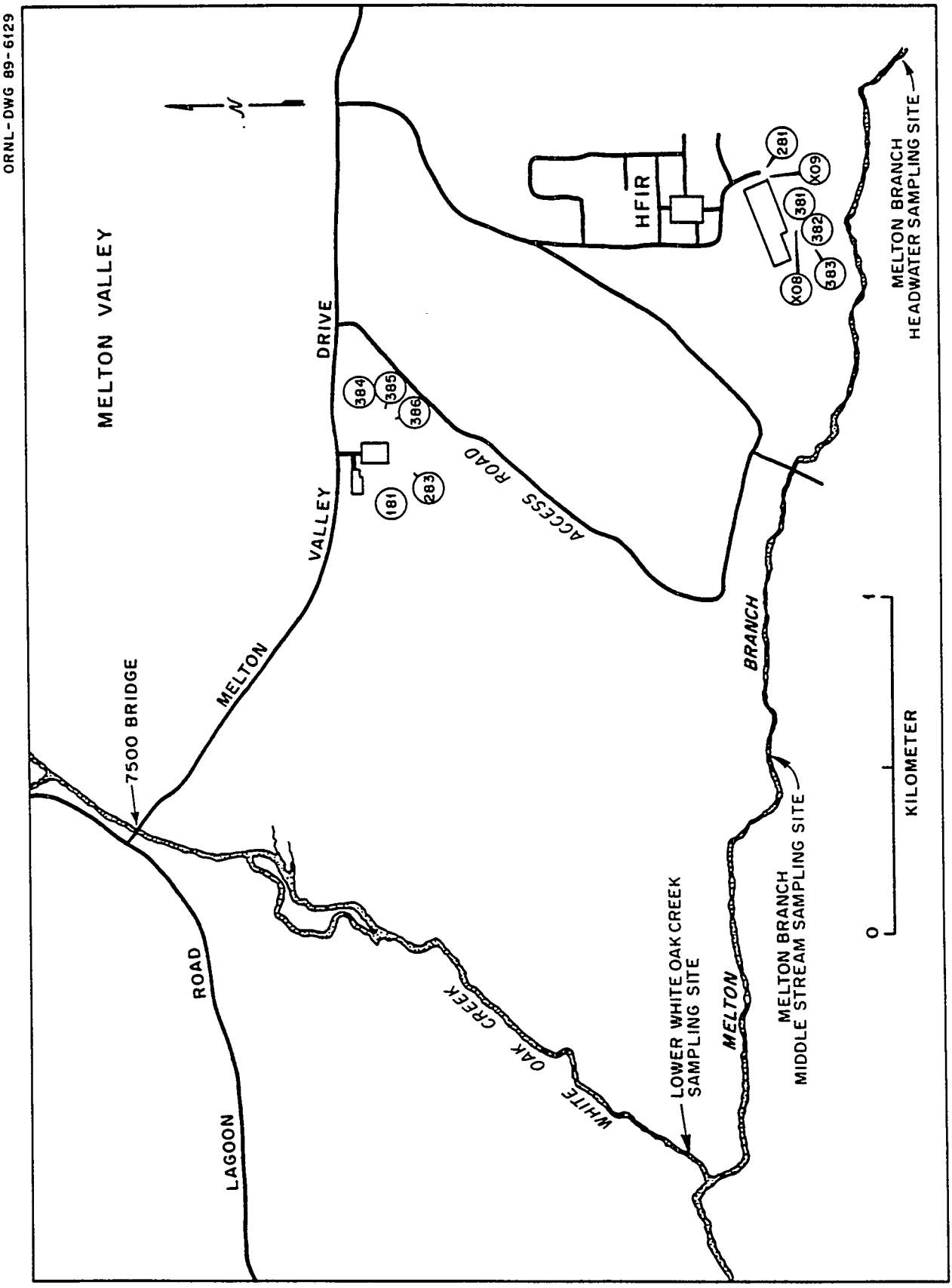

Fig. 2. Sampling stations in the ORNL Melton Valley complex. The circled numbers are positioned as near as possible to the outfall. Series number (100, 200, 300, or X) corresponds to the outfall categories identified in Tables 2–6.

Table 6. Summary of receiving waters outfall identifiers (number) and miscellaneous locations for mercury determinations[a]

Receiving water	Outfall or area to be sampled
White Oak Creek	101, 103, 106, 109, 116, 202, 204, 206, 207, 208, 209, 210, 216, 217, 218, 222, 223, 230, 232, 233, 234, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, X01, X02, X04, X06, X07, 7500 B, flume, headwaters, lower creek section, White Oak Dam
First Creek	141, 142, 143, 241, 243, 244, 246, 247, 248, 341, 342, 343, 344, X12
Fifth Creek:	161, 162, 163, 164, 261, 262, 265, 268, 361, 362, 363, 364, 365, 366, 367, 368
Melton Branch:	181, 281, 283, 381, 382, 383, 384, 385, 386, X08, X09, headwaters section, middle branch section, and Melton Hill Dam
Northwest Tributary	X03

[a]The actual number of outfalls sampled varied between sampling periods because some outfalls had no discharge.

5.0 SAMPLE COLLECTION

All water samples consisted of three replicate, manual grab samples collected during two sampling periods (dry and wet seasons) in 1988. Samples were collected in 1-L I-Chem high-density polyethylene bottles with teflon caps. I-Chem bottles are proprietary containers, precleaned by the vendor to EPA specifications where microdeterminations are requested. Samples were preserved immediately upon collection by acidifying with concentrated nitric acid to a pH of <2.0. Sediment samples were collected at selected stations and placed in glass containers. The glass containers were also I-Chem, EPA approved. Generally, samples were analyzed as soon as possible after collection, and no sample analysis exceeded the maximum allowable holding time of 28 days.

6.0 SAMPLE PROCEDURES, DATA MANAGEMENT, AND CONTROL

6.1 ANALYTICAL METHODS

Water and sediment samples were analyzed for total mercury content by manual cold vapor atomic absorption (USEPA, 1982). A modification of Method 245.1 (USEPA, 1983) was utilized for all analyses, and the results of sediment analyses were reported on a dry weight basis.

6.2 DATABASE MANAGEMENT SYSTEM

A computerized NPDES database exists on the Environmental Monitoring and Compliance Section's VAX computer. The database can be modified to maintain all records and allow for retrieval of records and data from all sampling and monitoring activities. The database permits tracking of all sampling sites and includes the date and time of collection, the identity of the individuals collecting each sample, and a description of how and under what conditions the sample was taken. Analytical data are transferred to the database by computer from entries verified by the laboratory supervisor in the Analytical Chemistry Division's computer. Hard copies also provide verification. The structure of the database is such that retrieval of information for risk assessment is possible.

6.3 QUALITY ASSURANCE

6.3.1 Sample Analysis

The validity of the sample analysis was demonstrated by the use of distilled water blanks to ensure that all glassware and reagents were interference-free. The blanks were carried through all stages of sample preparation and analysis. Blanks were used with each set of samples. All samples were analyzed within the prescribed time limits (28 days) noted previously.

6.3.2 Replicate Samples

Three replicate field samples were collected to ensure that sampling techniques were consistent and to identify the concentration variability at each station. Laboratory duplicates within samples were analyzed to assure precision of analysis.

6.3.3 Chain-of-Custody

A "DOE X-10 Plant Chain-of-Custody" form was completed and remained with the sample until the Analytical Chemistry Division assumed control of the sample. At that time, an "Analytical Chemistry Division Chain-of-Custody" form was initiated and remained with the sample until the analyses were completed. Any additional information or variation in standard procedures was noted in a laboratory notebook.

7.0 RESULTS

The analytical chemistry data (1987) were used to identify areas of elevated mercury concentrations and were combined with maps of drainage systems to form the basis of the sampling program. The key objective of the sampling effort is to assist management in reducing mercury discharges from identifiable sources and to provide a means to monitor the effectiveness of any prescribed remedial procedures through subsequent sampling and analysis.

7.1 SCOPING SURVEY 1987 (WATER)

The sampling stations in this study were not sited to illustrate a concentration gradient from the ORNL complex, but rather to identify those areas of suspected mercury sources. Concentration data for water are expressed in ng/mL (ppb), while data for sediment are reported in ug/g, dry weight (ppm). Data from the 1987 scoping survey identified four locations with evidence of elevated mercury concentrations. Two hundred and twenty-two samples were analyzed for 74 stations (Table 7). The headwaters of White Oak Creek served as the background concentration. Analytical data indicated a concentration of <0.5 ng/mL (n=3). The highest concentration identified along White Oak Creek was near Outfall 309, which receives discharges from Building 4500, the Central Research Complex, through Holding Basins 3539 and 3540. These basins have been in operation since 1964. The mean concentration near the Outfall 309 was 2.27 $\pm$ 0.38 ng/mL. Serial Numbered Outfall X06 is the NPDES monitoring station serving Basins 3539 and 3540 and is approximately 100 m from White Oak Creek. Discharge from X06 flows to the creek through Outfall 309. The mean concentration for X06 station was 0.73 $\pm$ 0.03 ng/mL. Because 309 is the final point in the effluent stream, the concentration would be expected to be less than the concentration observed at X06. The sample for Outfall 309 was collected as the discharge entered White Oak Creek and probably represents a mixed source.

Fifth Creek receives effluents from several process wastes (300 Series Outfalls). Notably among potential mercury sources are the discharges from Buildings 4501 and 4505, which historically supported activities which utilized an amalgam process. Those discharge concentrations did not exceed the White Oak Creek background concentration of <0.5 ng/mL. Outfall 261 supposedly receives water from roof drains, spill areas, storage area drains, and cooling water discharges. Most of the discharge through Outfall 261 is from the Building 3500 environs. This outfall depicted the highest mercury concentration (4.77 $\pm$ 0.18 ng/mL) of all stations sampled in the scoping survey. A mercury spill (Table 1) is recorded from Building 3500 but quantitatively (<0.2 kg) is insignificant to the water concentration observed. Sources other than Building 3500 are suspected to contribute mercury through this outfall.

Table 7. Summary of analytical data (water) for the 1987 scoping survey[a]

Outfall number/location	n	ng/mL ± 1 SE
	White Oak Creek	
106	3	<0.05
202	3	<0.50
203	3	<0.50
204	3	<0.50
207	3	<0.50
209	3	<0.50
210	3	<0.50
216	3	<0.50
217	3	<0.50
218	3	<0.50
222	3	<0.50
223	3	<0.50
230	3	<0.50
232	3	<0.50
233	3	<0.50
234	3	<0.50
243	3	<0.50
301	3	<0.50
302	3	<0.50
303	3	<0.50
304	3	<0.50
308	3	<0.50
309	3	2.27 ± 0.38
310	3	<0.50
311	3	<0.50
312	3	<0.50
313	3	<0.50
314	3	<0.50
7500B	3	<0.50
Flume	3	<0.50
WOD	3	<0.50
X01	3	<0.50
X02	3	<0.50
X03	3	<0.50
X04	3	<0.50
X06	3	0.73 ± 0.03
X07	3	<0.50

Table 7 (continued)

Outfall number/location	n	ng/mL ± 1 SE
	First Creek	
142	3	<0.50
143	3	<0.50
241	3	<0.50
243	3	<0.50
244	3	<0.50
247	3	<0.50
248	3	<0.50
341	3	<0.50
342	3	<0.50
243	3	<0.50
X12	3	<0.50
	Fifth Creek	
161	3	<0.50
162	3	<0.50
165	3	<0.50
261	3	4.77 ± 0.18
262	3	<0.50
268	3	<0.50
361	3	<0.50
362	3	<0.50
363	3	<0.50
364	3	<0.50
365	3	<0.50
366	3	<0.50
367	3	<0.50
368	3	<0.50
	Melton Branch	
181	3	<0.50
281	3	<0.50
283	3	<0.50
381	3	<0.50
383	3	<0.50
384	3	<0.50
386	3	<0.50
X08	3	0.60 ± 0.00

Table 7 (continued)

Outfall number/location	n	ng/mL ± 1 SE
	Miscellaneous	
White Oak Creek Headwaters	3	<0.50
White Oak Creek Lower Creek	3	<0.50
Melton Branch Headwaters	3	<0.50
Melton Branch Small Middle Branch	3	<0.50

[a]Data in boxes represent the most significant concentrations.

Melton Branch receives waste water from the High Flux Isotope Reactor complex and the Transuranic Processing Facility (7500 area). Serial Numbered Outfall X08 is the NPDES monitoring station for the various holding ponds, prior to discharge through Outfalls 381-386. The mercury concentration at X08 was 0.60 ng/mL or background.

7.2 SPRING SAMPLING 1988 (WATER)

In February of 1988, 61 stations were sampled for mercury concentrations. Each site consisted of three replications for a total of 183 samples (Table 8). The lower limit for data reported for this series of data is <0.1 ng/mL, in contrast to <0.5 ng/mL in 1987. The detection limit is a function of the aliquot volume utilized in the analyses and does not indicate a change in methodology. Only eight locations contained quantitative concentrations (mean ± 1 SE). Among those outfalls, 309 was the highest with a mean concentration of 2.10 ± 0.06 ng/mL. That concentration is essentially the same as measured in the 1987 survey and suggests a uniform input. The second notable concentration (1.17 ± 0.03 ng/mL) was from Outfall 367. Outfall 367 discharges into Fifth Creek east of Building 3036, the Isotope Area Storage and Service Building.

Table 8. Summary of analytical data (water) for the February 1988 sampling effort[a]

Outfall number	n	ng/mL ± 1 SE
	White Oak Creek	
106	3	<0.1
202	3	0.17 ± 0.07
204	3	<0.1
207	3	0.17 ± 0.03
210	3	<0.1
217	3	<0.1
218	3	<0.1
223	3	<0.1
230	3	<0.1
233	3	<0.1
234	3	<0.1
301	3	<0.1
302	3	<0.1
304	3	0.13 ± 0.03
305	3	<0.1
309	3	2.10 ± 0.06
310	3	<0.1
311	3	<0.1
312	3	<0.1
313	3	<0.1
314	3	<0.1
X01	3	<0.1
X02	3	<0.1
X04	3	0.5 ± 0
X06	3	<0.1
X07	3	<0.1
Flume	3	0.4 ± 0
7500B	3	0.2 ± 0
WOD	3	<0.1
	Fifth Creek	
161	3	<0.1
262	3	<0.1
265	3	<0.1
268	3	<0.1
363	3	0.17 ± 0.07
365	3	<0.1
366	3	<0.1
367	3	1.17 ± 0.03
368	3	<0.1

Table 8 (continued)

Outfall number	n	ng/mL ± 1 SE
	First Creek	
143	3	<0.1
247	3	<0.1
248	3	<0.1
341	3	0.5 ± 0
342	3	<0.1
343	3	<0.1
X12	3	<0.1
	Melton Branch	
181	3	0.13 ± 0.03
281	3	<0.1
381	3	<0.1
382	3	<0.1
383	3	<0.1
384	3	<0.1
386	3	<0.1
X08	3	<0.1
X09	3	<0.1
	Miscellaneous	
White Oak Creek Headwaters	3	<0.1
White Oak Creek Lower Creek	3	0.17 ± 0.03
Melton Branch Headwaters	3	<0.1
Melton Branch Small Branch	3	<0.1
Melton Hill Dam Melton Branch	3	<0.1
X03 Northwest Tributary	3	<0.1

[a]Data in boxes represent the most significant concentrations.

7.3 FALL SAMPLING 1988 (WATER)

In October of 1988, 88 locations were sampled for mercury concentrations. Each site consisted of 3 replications for a total of 264 samples (Table 9). The detection limit reported for this data set was <0.05 ng/mL. Most of the data reported were quantitative (fewer < values). Four locations were significant among the observations, with mercury concentrations >0.5 ng/mL. For example, Outfall 106 had an average concentration of 0.72 $\pm$ 0.03 ng/mL. This outfall enters White Oak Creek south of Building 4508, the Metals and Ceramics Laboratory, and 100 m east of the confluence with Fifth Creek. The discharge from this outfall is from the storm drain system along Southside Drive. Outfall 311 had a mean concentration of 0.70 $\pm$ 0.02 ng/mL. This outfall serves some process wastes from Building 4500S. Serial Numbered NPDES station X07 serves the Process Waste Treatment Plant (Building 3544). This facility potentially receives wastewater from the majority of the Laboratory's facilities, including Basins 3539 and 3540 and the 3524 Equalization Basin. Constituents that exceed discharge limits from the holding basins are transferred to the Process Waste Treatment Plant for treatment (rad reduction by clarifer and ionic exchange column and pH adjustment) prior to discharge into White Oak Creek. The mean mercury concentration was 0.70 $\pm$ 0.02 ng/mL during this sampling period. The highest mercury concentration noted was from Outfall 367 along Fifth Creek, near the Isotopes Area Storage amd Service Building (3036), with a mean of 1.87 $\pm$ 0.17 ng/mL. That compares with the spring sample concentration of 1.17 $\pm$ 0.03 ng/mL.

The Tennessee state standard (0.05 ug/L) is four times more stringent than the Federal standard (0.2 ug/L) for mercury in water. Much of the water chemistry data in this report exceed the Federal standard, while nearly all data exceed the state standard. This is not an indication of mercury contamination. The stream headwaters (background) concentrations exceed the state limit. Both standards are derived from literature abstractions from effects studies and do not reflect the state-of-the-art capabilities of analytical equipment.

7.4 MERCURY CONCENTRATIONS IN ORNL STREAM SEDIMENTS

Twelve sites were selected for mercury analyses in sediments. These sites were selected from previous water chemistry data, personal interviews with persons having knowledge of mercury spills at ORNL, and locations of suspected depositions of mercury. In 1982, (Van Winkle et al.) reported mercury concentrations among sediments of New Hope Pond (Y-12) and East Fork Poplar Creek. Shacklette et al., in 1971 indicated that the average concentration of mercury in sediments for the eastern conterminous United States was 0.147 ug/g. Mercury concentrations in clayey sediments in Cherokee Lake of East Tennessee have been reported to range from 0.6 to 2.5 ug/g (Turner and Lindberg, 1978). These latter data represent depositions from a mercury cell chloralkali plant. The sediment data for ORNL streams are presented in Table 10 and are not intended to infer a dilution with distance from the ORNL complex. For sediment data to be comparable, all materials must be sieved, with stones and organic materials removed. This was not the procedure with the sediments collected in this report. In fact,

Table 9. Summary of analytical data (water) for the October 1988 sampling effort[a]

Outfall number/location	n	ng/mL ± 1 SE
	Fifth Creek	
161	3	1.10 ± 0
162	3	0.10 ± 0
163	3	0.10 ± 0
164	3	0.13 ± 0.03
261	3	0.17 ± 0.07
262	3	<0.05
265	3	<0.05
268	3	<0.05
361	3	<0.05
362	3	<0.05
363	3	<0.05
364	3	0.10 ± 0
365	3	0.10 ± 0
367	3	1.87 ± 0.17
368	3	<0.05
	First Creek	
141	3	<0.05
142	3	<0.05
143	3	<0.05
241	3	0.10 ± 0
243	3	0.10 ± 0
244	3	0.10 ± 0
246	3	0.10 ± 0
247	3	0.20 ± 0
248	3	0.20 ± 0
341	3	0.23 ± 0.03
342	3	0.10 ± 0
343	3	<0.05
344	3	<0.05
X12	3	<0.05
	Melton Branch	
181	3	<0.05
281	3	<0.05
283	3	<0.05
381	3	<0.05
382	3	<0.05
384	3	<0.05
386	3	<0.05
X08	3	<0.05

Table 9. (continued)

Outfall number/location	n	ng/mL ± 1 SE
	Miscellaneous	
X09	3	<0.05
White Oak Creek Headwaters	3	0.1 ± 0
White Oak Creek Lower Creek	3	<0.05
Melton Branch Headwaters	3	<0.05
Melton Branch Small Middle Branch	3	<0.05
Melton Hill Dam Melton Branch	3	<0.05
	White Oak Creek	
101	3	0.2 ± 0[b]
103	3	0.2 ± 0
106	3	0.72 ± 0.03
109	3	<0.05
116	3	0.10 ± 0
202	3	0.20 ± 0
204	3	0.20 ± 0
206	3	0.20 ± 0
207	3	0.17 ± 0.03
208	3	0.20 ± 0
209	3	0.20 ±
210	3	0.10 ± 0
216	3	<0.05
217	3	0.13 ± 0.03
218	3	<0.05
222	3	0.13 ± 0.03
223	3	0.10 ± 0
230	3	0.10 ± 0
232	3	0.10 ± 0
233	3	0.10 ± 0
234	3	0.10 ± 0
301	3	0.10 ± 0
302	3	0.30 ± 0
303	3	0.27 ± 0.03
304	3	0.17 ± 0.03

Table 9. (continued)

Outfall number/location	n	ng/mL ± 1 SE
305	3	0.30 ± 0
306	3	0.20 ± 0
307	3	0.10 ± 0
308	3	0.10 ± 0
309	3	0.10 ± 0
310	3	0.20 ± 0
311	3	0.70 ± 0.02
312	3	0.10 ± 0
313	3	0.20 ± 0
314	3	0.13 ± 0.03
7500B	3	0.10 ± 0
FLUME	3	0.20 ± 0
WOD	3	<0.05
X01	3	<0.05
X02	3	0.30 ± 0
X03	3	0.30 ± 0
X04	3	0.17 ± 0.03
X06	3	0.23 ± 0.03
X07	3	0.70 ± 0.02
X11	3	0.30 ± 0

[a]Data in boxes represent the most significant concentrations.

[b]0 standard error indicates all three replications had the same concentration.

the data may be viewed as minimal since the samples were not fractioned, and a small stone in an analytical aliquot could have a significant dilution bias.

New Hope Pond was sampled (Van Winkle et al., 1984) from a 0 to 95 cm depth for total mercury analyses. The intent of the vertical profile was to determine whether mercury deposition had been a continuous pathway for accumulation or if there existed discrete periods (spikes) of deposition. The data revealed that mercury increased with depth (time), reaching a maximum concentration at a depth of 70 to 75 cm. The lower concentrations at 0-5 cm deep suggested a reduction in mercury deposition in recent years. East Fork Poplar Creek receives stream flow from New Hope Pond. Mercury concentrations for surface sediments ranged from 19 to 127 ug/g at 2.1 and 22.2 km downstream from New Hope Pond, respectively.

The data for ORNL streams range from background (0.13 ± 0.02) in White Oak Creek Headwaters to a maximum of 4874 ± 2556 ug/g below Outfall 261 into

Fifth Creek. A summary of spatial mercury contamination in sediments of ORNL streams is presented in Table 10 and Fig. 3. While some of these concentrations appear to be alarming, it must be cautioned that the potential source plume is probably 0.5 m wide at its maximum width and extends an estimated 1.5 m. As an example, the sediment plume from Outfall 261 is 1 m long and 20 cm wide. The samples were collected to 5 cm deep. Considering a sediment bulk density of 1.4 g/cm^3 and the average mercury concentration of 4874 ug/g, it is estimated that a maximum of 68 g of mercury may be present. The sediment analyses identify sources of mercury which likely contribute to elevated stream concentrations. Mercury input into streams increases during high rainfall runoff events (Van Winkle et al., 1984). The concentration (22.26 ug/g) observed near Outfall 309 most likely reflects input from the Central Research Complex, Building 4500, whereas the concentrations along Fifth Creek reflect past spills from the lithium isotope separation/uranium-thorium metal production processes. The highest concentration (4874 ug/g) from Outfall 261 indicates a source from Building 3500 or other nearby facilities. The concentration (2.69 ug/g) in Melton Branch before joining White Oak Creek suggests the Solid Waste Storage Area (SWSA) 5 as a potential source.

8.0 CONCLUSIONS AND RECOMMENDATIONS

The water chemistry data are supported by the sediment data in identifying sources of mercury to ORNL streams. The sediment analyses indicate surface (0-5 cm) contamination only. However, to ascertain whether imput to these areas is continuous, depth (cores) profile analyses are recommended. In addition, core studies should be initiated along a horizontal dimension to define the configuration of the source plume (sediments) and to suggest possible remedial actions to reduce these sources of mercury.

Both water and sediment sampling should be continued to determine the success of any remedial action and to identify any new source, should one appear.

Table 10. Summary of mercury concentrations (ug/g) in sediments from ORNL streams

Location	n	Concentration ± 1 SE
White Oak Creek Headwaters	3	0.13 ± 0.02
Fifth Creek Outfall 362 Box	3	21.10 ± 7.57
Fifth Creek Below Outfall 362	3	67.53 ± 26.78
Fifth Creek Near Outfall 261	3	4874 ± 2556
White Oak Creek Upstream of Fifth Creek	3	5.39 ± 0.70
White Oak Creek Near Outfall 309	3	22.20 ± 6.17
Northwest Tributary Upstream First Creek	3	0.17 ± 0.03
First Creek Upstream of Northwest Tributary	3	0.67 ± 0.29
White Oak Creek Downstream First Creek	3	8.93 ± 0.66
White Oak Creek Upstream Melton Branch	3	0.31 ± 0.08
Melton Branch at MBR2 Weir	3	0.53 ± 0.07
Melton Branch Upstream of White Oak Creek	3	2.73 ± 0.34

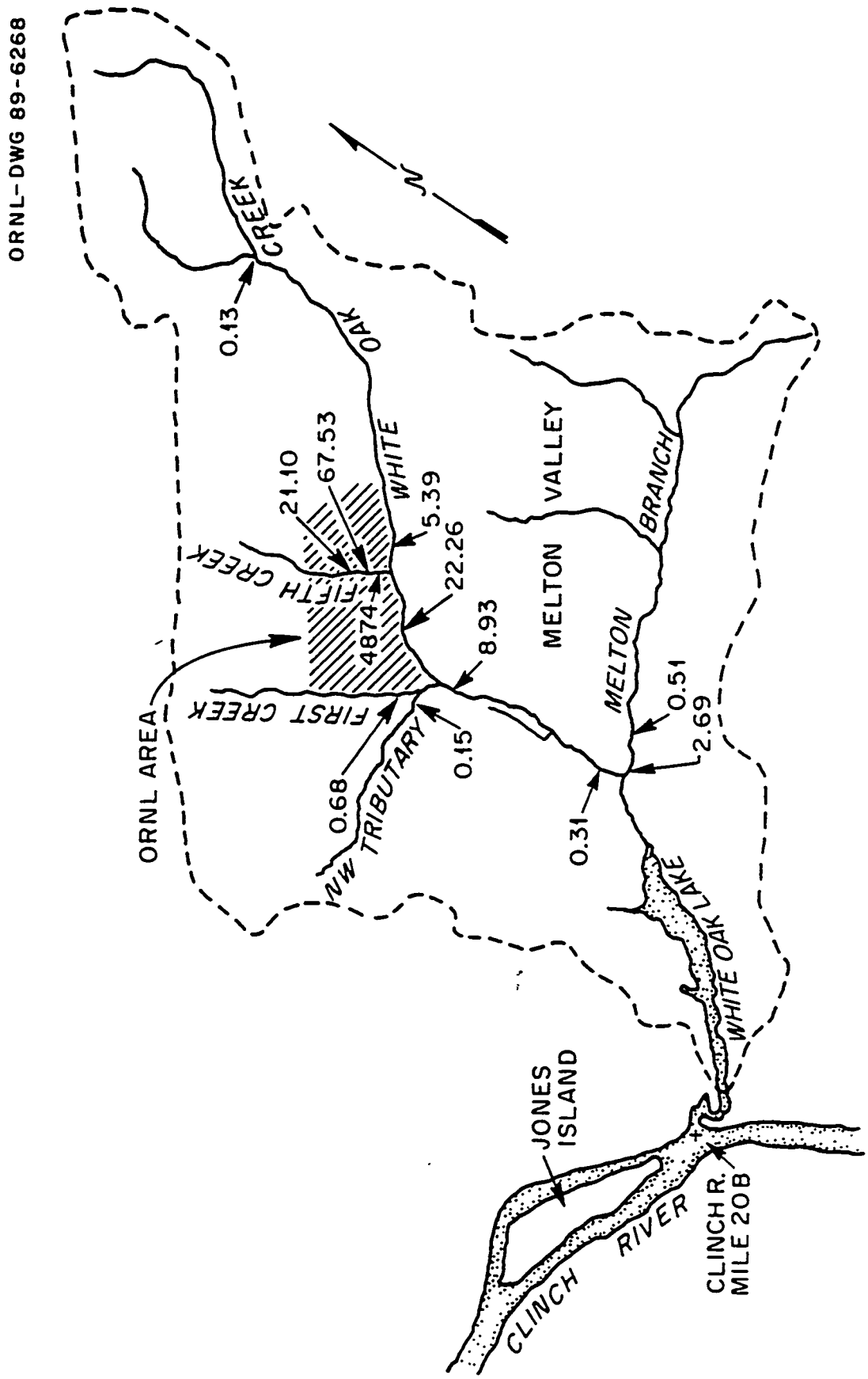

Fig. 3. Locations in ORNL streams with excess mercury concentrations in sediments. Statistics are summarized in Table 10.

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Remedial Investigation Plan for ORNL Waste Area Grouping 1

Oak Ridge National Laboratory
Remedial Investigation/Feasibility Study

REVISION 1

August 1989

U.S. Department of Energy
Oak Ridge Operations Office

Prepared by

Bechtel National, Inc.
CH2M Hill • EDGe • PEER

for

Oak Ridge National Laboratory

Operated by

Martin Marietta Energy Systems, Inc.

Susan FYI Regarding Hg at X-10

* chk. the doc. w the X-10 Hg release estimate

3517 Filter Pit (Fission Product Development Laboratory - Building 3517) (SWMU 1.20)

The filter pit east of Building 3517 was put in service in 1958 to filter building air exhaust from the Fission Product Development Laboratory (FPDL). The stainless steel roughing filters were acid-backwashed, and the leakage from this operation has contaminated the filter pit. During recent excavations at the site large quantities of contaminated soil were removed. The principal contaminants are cesium-137 and strontium-90.

FPDL LLW Transfer Line (SWMU 1.21)

The line was installed in 1958 and taken out of service in 1978. Wastes are currently transferred to a collection header on the west side of the South Tank Farm. No leaks have been reported. The inactive line is reported to be contaminated with cesium-137 and strontium-90 but no inventory information is available.

Isotopes Ductwork/Building 3110 Filter House (SWMU 1.22)

This filter house serves the cell ventilation air exhaust in the isotopes area. A floor drain in Building 3110 collects groundwater and transports it to Tank WC-10. Groundwater leakage into the underground air duct system also accumulates and is collected in a sump for transfer to the process waste system. This site has been removed from service.

3.2.2.2 Chemical Leaks and Spills. A brief description of each of the chemical leaks and spills is provided below.

Mercury-Contaminated Soil - Building 3503 (SWMU 1.1)

During the 1950s and early 1960s, substantial quantities of mercury were used in the spent fuel reprocessing program known as PUREX.

information exists on the quantity of possible losses. Analysis of soil samples collected from various locations around Building 3503 has indicated quantities of mercury ranging from 0.8 to 25 ppm.

Mercury-Contaminated Soil - Building 3592 (SWMU 1.2)

During 1956, supporting equipment development work was performed in Building 3592 in conjunction with the research activity on lithium separation. Over a period of about 2 months, more than 60,000 lb of mercury was used. No record of the amounts lost through spills is available; however, operating personnel have estimated that a total of 2000 to 3000 lb of mercury was lost through spills and leaks. Analysis of soil samples taken in 1983 from various locations around 3592 showed mercury concentrations ranging from 4.1 to 320 ppm.

Mercury-Contaminated Soil - Building 4501 (SWMU 1.3)

For about 6 months during 1954, ton quantities of mercury were used at Building 4501 for the operation of a small pilot plant for lithium separation (OREX process). Spills did occur. During a spill the visible mercury was cleaned up, but some escaped into cracks in the concrete floor. Currently the building is used as a high-level radiochemistry laboratory. Analyses of soil samples collected in 1983 from various locations around Building 4501 indicated concentrations of mercury ranging from 0.05 to 465 ppm.

Mercury-Contaminated Soil - Building 4508 (SWMU 1.4)

Although research activities in Building 4508 are reported to have used inventories of less than 100 lb of mercury, there is no information available to indicate that a mercury spill has occurred. No soil sampling has been conducted around Building 4508.

with other types of lines. Figures 3-12 through 3-14 show the locations of the storm sewer outfalls. The outfalls are numbered as members of the 100, 200, or 300 series. The 100 series drains only rainwater; the 200 series drains buildings and parking lots but no process effluent; and the 300 series drains buildings and areas where the presence of untreated process wastes is indicated. Flow volumes for the storm water sewer system are dependent on precipitation.

Water samples are collected and analyzed regularly from a number of stations in the WOC and its tributaries in WAG 1. Water is also sampled at the STP and the PWTP as well as in the 3500 area ponds.

Figure 3-15 shows locations of the surface water sampling stations in WAG 1 and vicinity. Table 3-13 is a summary of collection and analysis frequencies of the surface water samples. Table 3-14 shows the radionuclide concentrations in WOC and its tributaries for 1986. It appears that major sources of strontium drain toward First Creek. Considerable dilution occurs in WOC at the 7500 bridge.

A mercury assessment program was implemented in 1988 to identify, locate, and minimize all sources of mercury contamination in ORNL discharges to maintain compliance with the NPDES permitting program (Taylor, 1989) (Figure 3-15a). Surface water samples were collected from selected NPDES outfalls (Categories I, II, and III) and from previously established serial numbered sampling stations, these were submitted for mercury analysis.

The results of this survey indicated several areas with mercury levels significantly above background levels: 1) a storm drain outfall (No. 106) along Southside Drive which enters White Oak Creek south of Building 4508 (Figure 3-15a); 2) the process waste outfall (No. 311) from Building 4500S; 3) the monitoring station (X07) along White Oak Creek serving the PWTP; 4) Outfall No. 36

(Rev.

along Fifth Creek near Building 3036; 5) Outfall No. 261, which discharges to White Oak Creek and receives runoff from roof drains, spill areas, and cooling water discharges from the Building 3500 area; and 6) Outfall No. 309 which receives discharges from Building 4500S through Holding Basins 3539 and 3540 and discharges to White Oak Creek.

Stream gravel surveys in the WOC watershed were conducted by Cerling and Spalding (1981) to define the areal distribution of cobalt-60, cesium-137 and strontium-90. Later studies (Cerling and Huff, 1986; Morrison and Cerling, 1987) corroborated the general findings of the earlier study. Figure 3-16 gives the locations of sediment sampling points including those within the WAG 1 area used by Cerling and Spalding.

Table 3-15 gives the ranges of concentrations of various radionuclides found in WOC, First Creek, and Northwest Tributary sediments (Fifth Creek sediments were not sampled).

The principal source of cesium-137 is the PWTP. The principal sources of strontium-90 are direct ORNL plant effluents, and cooling water effluent from the High Flux Isotope Reactor is the dominant

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DATE: February 18, 1953

TO: K. Z. Morgan

FROM: W. J. Lilley

SUBJECT: OREX TEST FACILITY WASTE DISPOSAL

A meeting was held on February 12, 1953 to discuss the disposal of waste material from the Orex Test Facility. The following were present:

W. J. Lilley - Process Design Section, Chemical Technology Div.
R. J. Morton - Health Physics
O. R. Placak - USPHS

The specific purpose of the meeting was to examine the possibility of disposing waste materials directly into White Oak Creek through storm drains located at the Orex Test Facility site. The waste stream is proposed to be a continuous flowing neutral aqueous stream containing both magnesium and sodium sulfates, sodium chloride with small amounts of propylenediamine and benzene. The foreseen concentration of the above materials in both the White Oak Creek and Clinch River are as shown on the attached Table I. The waste stream is to be controlled to a pH ranging from 6.0 to 7.0.

It was concluded that the above inorganic salts did not present a contaminating condition throughout the White Oak Creek, and Clinch River systems. Further the maximum predicted concentration of propylenediamine and benzene represents a border line case that would have to be further investigated before recommendation could be made.

It was recommended that a "scanning type" test be made on this material by the Health Physics Department. The results of these tests should quickly indicate whether the Test Facility waste materials can be disposed of in this manner. Should these results still indicate a border line condition, further testing may be carried out by the USPHS at Cincinnati, Ohio.

Following these recommendations we are submitting to you two, one quart samples of the waste stream containing the combined waste concentration as produced under normal operations. These samples will have to be diluted with water to conform with the total concentration as shown on Table I. It should be noted that propylenediamine has not been

[redacted]

found in any of the waste material made from laboratory experimental runs. Therefore, one sample contains a solution made up from salts produced from experimental runs on the desolvation step and the other is made up synthetically containing the maximum predicted quantity of propylene diamine.

Your recommendation on the matter will be appreciated.

Walter J. Lilley
Process Design Section
Chemical Technology Division

WJL/es

[redacted]

[redacted]

TABLE I

PREDICTED CONCENTRATION OF WA
FROM THE OREX TEST FACILI
(Figures in ppm)

Component	Desolvation Section				Solvent Drying Section		
	In White Oak Creek (1)		In Clinch River(2)		In White Oak Creek		In Clin Rive
	Start Up	Normal Oper	Start Up	Normal Oper.	Start Up	Normal Oper	Start Up
$MgSO_4$	-	386	-	1.0	-	-	-
NaCl	-	397	-	1.0	-	-	-
Na_2SO_4	-	398	-	1.0	-	-	-
PDA(3)	-	28.9	-	0.1	8.0	4.0	0.03
Benzene	-	-	-	-	2.0	1.0	0.007
pH	-	6-7	-	7.0	7.0	7.0	7.0

(1) Basis 500 GPM flow

(2) Basis 500 CFS flow

(3) Maximum predicted value of propylenediamine

[redacted]

\STE STREAM
:TY

	From Floor Washing				Total			
	In White Oak Creek				In White Oak Creek		In Clinch River	
:h Normal Oper	Start Up	Normal Oper.	Start Up	Normal Oper.	Start Up	Normal Oper.	Start Up	Normal Oper
-	-				-	386	-	1.0
-	-				-	397	-	1.0
-	-				-	398	-	1.0
0.01	8.0	4.0	0.03	0.01	16.0	37.0	0.06	0.12
0.003	-	-	-	-	2.0	1.0	0.007	0.003
7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0

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W. R. Carroll
Chief, Declassification Branch

March 12, 1953

To: W. J. Lilley, Chemical Technology Division

From: K. Z. Morgan, Health Physics Division

Subject: OREX TEST FACILITY WASTE DISPOSAL

Your letter of February 17, 1953, dealing with "OREX Test Facility Waste Disposal" has been under discussion by Messrs. Roy J. Morton, L. A. Krumholz, O. R. Placak and C. P. Straub. This letter was sent in compliance with the official bulletin from Dr. C. E. Larson to all supervisors (AR - 142) dated September 26, 1950. In the discussions you have had with the above-mentioned persons, it has been pointed out that there are three main problems involved in the disposal of this chemical waste:

1. The effect on the water supply for drinking purposes, irrigation, and manufacturing.

2. The effect on the fish population in the Clinch and Tennessee River systems.

3. The effect on all plant and animal life in White Oak Lake, which is the laboratory for our Ecological Program.

I am enclosing copies of memoranda from Messrs. Morton, Straub and Krumholz, and I believe they summarize the information relating to these three problems and indicate our position in this matter. In short, the dilution factors are such that the likelihood of difficulty from problem No. 1 is extremely remote. Likewise with reference to problem No. 2 the dilution factors are such that no damage is expected to fish life in the Clinch and Tennessee River systems. With reference to problem No. 3, however, Dr. Krumholz points out clearly that this concentration of chemicals in White Oak Lake would be expected to destroy the fish life and completely upset the ecological balance, so that the Ecological Program would have to be discontinued for an indefinite period.

[redacted]

[redacted]

Attachment No. 1 to
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MEMORANDUM

March 3, 1953

To: K. Z. Morgan

From: Roy J. Morton

Subject: ORNX Test Facility Waste Disposal

It has been proposed that the waste materials from this facility be disposed by discharge into White Oak Creek. The Health Physics Division has been requested to give approval for the discharge of all of these wastes to the Creek or to recommend the extent of such discharges that will be acceptable.

Data and general information regarding the expected composition and quantities of the wastes from these tests and the foreseen concentrations in White Oak Creek and in Clinch River at times of low stream flow have been made available in discussions and memoranda including the following:

(1) Preliminary discussions by W. J. Lilley and others with C. P. Straub and K. Z. Morgan.

(2) Meeting February 12, 1953 - W.J. Lilley, R.J. Morton, and O.R. Hancok.

(3) Memorandum dated February 18, 1953 to K.Z. Morgan from W. J. Lilley (CF 53-2-163).

(4) Memorandum dated February 27, 1953 to K.Z. Morgan from C.P. Straub (copy attached).

(5) Meeting February 27, 1953 - W.J. Lilley, J.W. Boyer, R.J. Morton, and L.A. Krumholz.

Proposal for Discharge of Wastes to White Oak Creek

In summary, it appears that the following points are pertinent in the consideration of this proposal by the Health Physics Division.

1. General Information. - The proposal as discussed refers only to a specifically planned series of tests starting early in July, 1953 with a total of about 90 days of 24-hour per day operation. From the meeting on February 27 it is understood that this test is not for pilot plant process development to be scaled up later here or elsewhere. Other possibilities for the disposal of these wastes such as waste processing and drying, disposal into specially constructed pits, or collection in drums for storage or burial have been mentioned but were not discussed in detail. One alternative proposal for hauling and discharging the liquid wastes into an existing excavation is discussed in this memo.

[redacted]

The Ecological Program has been under the direct supervision of the Tennessee Valley Authority and perhaps this is one of two reasons why we should consult this agency before going ahead with plans to dispose of these large quantities of chemical waste in White Oak Creek. In short, we have a twofold responsibility to TVA:

1. Because they are directly responsible for the ecological studies in White Oak Lake, and

2. There is a regulation requiring that the TVA be consulted in matters pertaining to the impoundment of contamination of water systems in the TVA drainage area.

From the standpoint of the Health Physics Division, we have quite a stake in the Ecological Program, having invested many man-hours in this study since White Oak Lake probably offers the best research facility in the world for studying slow and progressive changes in the ecological environment due to the presence of low levels of radioactive contamination over periods of many years. Dr. Krumholz and personnel of his staff from our Laboratory and TVA are now in the process of writing up this information and making recommendation as to the future course of this program.

Mr. Morton points out several alternate methods of disposal of this chemical waste. If it would be possible to concentrate the waste at the source, from our point of view this would offer the simplest solution. Otherwise, it would seem most appropriate to place this liquid in an open pit from which it could drain slowly either into the White Oak Lake or directly into the Clinch River. The present pits for radioactive solutions should not be used for this purpose because this method of disposal is still in the experimental stage, and if it proves successful will involve a saving of many hundreds of thousands of dollars not only here but perhaps at other Laboratories and we would not wish to interfere with these studies. However, open pits possibly could be constructed in the general vicinity of the present radioactive waste pits so that the pipe line which is to be constructed to this waste area could be used alternately for the transportation of radioactive waste and the transport of chemical waste. The other possibility, of course, would be to transport the chemical waste by means of our presently existing tank truck.

Although this is not a radiation problem, I appreciate your calling it to our attention in conformance with the above mentioned letter from Dr. Larson. Not only do we have a personal interest because of our Ecological Program, but we have in our Division outstanding men in the sanitary engineering profession and representatives from the Public Health Service, who are anxious and willing to offer any assistance within their power on such problems. If we can be of further help, please do not hesitate to call on us.

Original Signed By
K. Z. MORGAN

KZM:mof
Encl. (3)

Karl Z. Morgan, Director
Health Physics Division

cc: L. A. Krumholz
R. J. Morton
C. P. Straub
F. L. Steahly
R. P. Milford
P. L. Culler
Morgan (2)

2. Concentrations of particular materials that might be expected in White Oak Creek and Lake and in Clinch River after discharge and dilution. Data regarding these concentrations are summarized in the table attached to the memo by W.J. Lilley and are analyzed and discussed in the memo by C.P. Straub.

3. The effects of the expected concentrations of the various materials in the Creek and Lake and in Clinch River, particularly the effects of increased inorganic salts and hardness in the water and of possibly toxic materials. As pointed out in the memo by C.P. Straub adequate information is not available regarding the effects of the relatively high concentrations that may be expected in White Oak Creek.

4. Over-all policy and implications. The question here is whether White Oak Creek should be used for the disposal of large quantities of materials from various sources without adequate data for an evaluation of the specific, general, and public relations effects that may result from the aggregate of all such discharges.

The sanitary engineering aspects of this proposal have been considered carefully by O.H. Placak, C.P. Straub and the writer. These aspects include potential effects upon human health - particularly adverse effects upon the K-25 and downstream water supplies, and any objectionable conditions in public streams or other waters which might make such waters less desirable or interfere with their uses. The purpose of this memorandum is to summarize for you our conclusions and viewpoints regarding this proposal. These comments are based upon the data made available and would not apply for increased discharges of these or similar materials.

In brief our conclusions are:

1. The proposed discharges would not cause health hazards in White Oak Creek or Lake because the water is not accessible to the public nor used by the public. If the Creek and Lake were public waters, we doubt seriously whether the proposed discharges could be permitted because of the increase in inorganic salts and hardness and the border-line concentrations of possibly toxic materials.

2. We would anticipate no health problems in Clinch River as a result of the proposed discharges because the concentrations of the various materials after dilution in the river are very low (less than five parts per million of inorganic materials and less than two-tenths parts per million of the possibly toxic materials).

3. No significant effects other than potential health hazards would result after dilution in Clinch River because, as mentioned above, the concentrations of the various materials in the river water will be very low.

4. Effects in White Oak Creek and Lake other than potential health hazards constitute a special problem of the Division and the Laboratory which depends upon the conditions and usage that are to be maintained in these Laboratory waters and the over-all policy regarding the indiscriminate use of White Oak Lake as a waste disposal facility.

We feel that there are certain related considerations and viewpoints which may be summarized as follows:

(1) In view of the increasing importance of stream pollution control and of water conservation for industrial and domestic use generally, consistent efforts should be made to prevent any needless contamination of streams even though in a particular case immediate adverse effects may not be foreseen.

(2) Although apparently not involved in the present proposal, we feel that in studies for the development of industrial processes the feasible methods and the economics of waste processing and disposal should be included as an inherent part of the development project.

(3) In the interest of public relations we should be conservative in the discharge of pollutional materials to streams in order to avoid suspicion or ill-will on the part of the general public and sportsman's groups and also to conform with the stated aims and requirements of regulatory agencies particularly of the Tennessee Stream Pollution Control Board.

Alternative Proposal

In order to avoid the discharge of wastes from this facility into a stream it was suggested on March 3, 1953 that the liquid waste be neutralized, hauled in a tank truck, and discharged into an existing shallow excavation located approximately one-quarter mile northwest of White Oak Dam and about the same distance north of the mouth of White Oak Creek. This area has been used for stripping top-soil and is accessible by a road which would require minor resurfacing. Regrading and the construction of low dikes could provide shallow pits of sufficient capacity to contain all of the wastes expected to be produced by this test facility. It was viewed by W.J. Lilley and others and also by the writer accompanied by L.A. Krumholz.

From cursory examination it appears that this proposal is feasible and can be made satisfactory. The preparation of the pit should be done in such a way that there would be no danger of flooding or overflowing of the pit with surface water following rains and no possibility of a washout of the retaining dikes so as to release all of the accumulated wastes as a slug into White Oak Lake embayment or into Clinch River.

If disposal into pits in this area is adopted, it is suggested that the pit be designed for a liquid depth of not more than about three feet and that a total waste volume of 500,000 gallons or 67,000 cubic feet be anticipated.

We visualize that the pit should be regraded to provide approximately 20,000 square feet of storage area enclosed by dikes which would contain the wastes and protect against major surface drainage from the surrounding areas. Other existing pits or the construction of a pit at a suitable location within the controlled area might be considered since hauling of the wastes to a disposal site now appears to be practicable.

Roy J. Morton

Roy J. Morton, Leader
Waste Disposal Research Section
Health Physics Division

cc: H. J. Milley
R. J. Morton - O. R. Placak
L. A. Krumholz
C. P. Straub
H. P. Milford
F. L. Culler
F. L. Steahly

Attachment No. 2 to CF [redacted].

[redacted]

INTER-COMPANY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY

(INSERT NAME) COMPANY ____ LOCATION Post Office Box P, OAK RIDGE, TENN.

TO K. Z. Morgan
LOCATION

ATTENTION
COPY TO

DATE February 27, 1953

ANSWERING LETTER DATE

SUBJECT OREX Test Facility Waste Disposal

Reference is made to the memorandum by W. J. Lilley of February 18, 1953, regarding the disposal of wastes from the Orex Test Facility.

For approximately the past 9 years the channel of White Oak Creek has served as an open drain for chemical and other wastes from the X-10 facility. At the present time those chemical wastes are of such magnitude that they have largely eliminated all plant and animal life from that water between the plant site and White Oak Lake. Any further wasting of relatively large volumes and concentrations of chemicals as those mentioned for the Orex Process would probably eliminate all living forms from White Oak Creek, and in time would render White Oak Lake uninhabitable for such forms as are living there now.

A sample of water taken from White Oak Creek near the Haw Gap bridge on February 26, 1953 was analyzed by personnel of Building 3504 as follows:

Total hardness	126 ppm
Alkalinity	94
Total solids	206 ppm
pH	7.4

Estimates of the normal operation of the Orex Test Facility indicate that a total of 1,184 ppm of dissolved inorganic salts along with 38 ppm of organic solvents of unknown toxicity will be added to the above concentration. Thus, at the flow rate mentioned in your memorandum, the Orex Test Facility will increase the chemical load in White Oak Creek about fivefold. Any decrease in flow rates would cause an increase in concentrations.

Also, on February 26, 1953, a rapid survey of the bottom fauna living in White Oak Creek indicated that the stream between the Settling Basin and Haw Gap was virtually devoid of animal life. Only a few of the very tolerant invertebrate forms were found and no fish were taken by seining. The number and variety of organisms increased progressively downstream (largely because of dilutions from the tributaries) to the point where Melton Branch enters White Oak Creek. As a means of comparison, samples comparable to those taken from White Oak Creek were taken from the tributaries to White Oak Creek.

[redacted]

Those tributaries are considered as the best sources of comparison because of their similarity in drainage and topography. None of these tributaries receive any chemical or radioactive effluent from the X-10 facility so far as is known. A comparison of the bottom fauna from White Oak Creek and Melton Branch follows:

White Oak Creek

Organisms	Below Settling Basin	Stream Gage	Melton Branch
Stoneflies	1	2	1
Mayflies	0	5	62
Caddisflies	0		23
Chironomids	0	Many	1
Other diptera	1		1
Dragonflies	0		2
Oligochaetes	0		4
Tubifex	Few	Many	
Snails	0	1	2
Crustaceans	0		9
Leeches	0	1	

From the evidence available, there is little doubt that the paucity of the bottom organisms in White Oak Creek is caused by the high chemical concentration and is not due primarily to the presence of radioactive materials or to silt deposits. There is an abundance and diversity of animals living in the retention pond near the Settling Basin. That retention pond area normally carries concentrations of radioactivity of approximately 2,000 or more c/m/ml, whereas the amounts of radioactivity in the effluent from the Settling Basin are considerably less than those in the retention pond. So far as the silt deposits are concerned, a survey of the area of White Oak Creek immediately in back of the 4500 area indicates that the bottom organisms in that area are relatively abundant when compared with the area between the Settling Basin and Haw Gap. Furthermore, fish have been observed in that region behind the 4500 area on several occasions in the past few months.

RP Milford
FL Culler
Krumholz (2)

cc: R. J. Morton
C. P. Straub
W. J. Lilley
F. L. Steahly

L. A. Krumholz

[redacted] CF [redacted]

INTER-COMPANY CORRESPONDENCE

(INSERT NAME) COMPANY OAK RIDGE NATIONAL LABORATORY CARBIDE AND CARBON CHEMICALS CORP. LOCATION Post Office Box P OAK RIDGE, TENN.

TO Karl Z. Morgan, Director,
LOCATION Health Physics Division, ORNL

DATE February 27, 1953

ANSWERING LETTER DATE

ATTENTION
COPY TO

SUBJECT FDA Waste Problem

From: Conrad P. Straub, Sr. San. Engr. U.S. Public Health Service,
Health Physics Division, ORNL

Through: Oliver H. Placak, Sr. Scientist, USPHS, and Roy J. Morton, Leader,
Radioactive Liquid Waste Research and Development Section, Health
Physics Division, ORNL.

On February 9, 1953, the following data were made available to the writer as to the quantities of chemicals to be discharged in the FDA process pilot plant (so-called herein for lack of a more specific name):

Chemical	Quantity Discharged lbs/hour	lbs/day
$MgSO_4 \cdot 7H_2O$**	196	4,700
NaCl	99	2,380
$Na_2SO_4 \cdot 10H_2O$***	227.5	5,460
FDA	7.2	173
H_2O	771.8	18,500*

*Or 2,160 gals/day
**To obtain quantity of $MgSO_4$ discharged multiply values by 0.4884.
***To obtain quantity of Na_2SO_4 discharged multiply values by 0.4405.

It is presumed that the wastes will be discharged into White Oak Creek, where they will be diluted with the total volume of liquid flowing therein, including settling basin discharges, before passage into White Oak Lake. From data available to us from the Operations Division, the average daily settling basin flow ranges from approximately 0.545 to 0.712 million gallons (February 1 through February 11, 1953 data) and during prolonged dry weather the settling basin effluent represents the bulk of the flow in White Oak Creek.

[redacted]

[redacted]

Curves have been prepared to show the variation in concentration with variation in total flow for each of the constituents noted above. Concentrations corresponding to flows of 10 gpm (gals/min), 100 gpm, and 1,000 gpm are given below:

Flow		Concentration in mg/liter(ppm - parts/million)*			
gpm	mgd	$MgSO_4 \cdot 7H_2O$	NaCl	$Na_2SO_4 \cdot 10H_2O$	PDA
10	0.014	39,200 (34,100)**	19,840 (17,250)	45,500 (39,600)	1,445 (1,253)
100	0.144	3,920 (3,860)	1,984 (1,956)	4,550 (4,490)	144.5 (142.3)
1,000	1.44	392 (390)	198.4 (197.6)	455 (454)	14.45 (14.38)

*It is assumed that complete mixing occurs and that the chemical constituents are uniformly distributed throughout the receiving stream.

**Values in ( ) represent concentrations which result when the 2,160 gpd of process water (see first tabulation) is added to the dilution water volume and represents the total volume available for dilution.

The reported flow volumes of 0.545 to 0.712 mgd are within the ranged considered in the above table.

In my memorandum of December 17, 1952 to Dexter W. L. Carter entitled Toxicity of Magnesium Chloride and Propylenediamine to Fish", it was reported that no data were available on the toxic concentration of PDA, but if its toxicity were comparable to that of related amines, a value of 30 to 60 ppm of PDA could tentatively be accepted as representing the toxic level for fish, until such time as laboratory studies made with PDA proved otherwise.

Data available on the toxic levels of sodium sulfate, Na_2SO_4, indicate that 500 ppm in tap water was not injurious to goldfish in 24 hours (Haruksen, 1922) and that 7,105 ppm in Lake Erie water immobilized Daphnia magna, a fresh water cladoceran (Andersen, 1944). Wiebe, Burr, and Faubion (1934) indicate that 5,000 ppm NaCl in distilled water killed golden shiners, Notemigonus crysoleucas, in 148 hours and largemouth black bass in 200-250 hours. Anderson (1944) reports that 6,143 ppm NaCl immobilized Daphnia magna in Lake Erie water. No information is available on the effect of $MgSO_4$ on fish. It will be noted that these values represent only the individual salt and its toxic effect. No data are available on the toxicity of mixtures of these particular salts.

[redacted]

To note the effect of these chemicals (exclusive of PDA) on the hardness and pH of White Oak Creek water, an experiment was set up using a waste stream having characteristics similar to those of a composite sample of settling basin effluent collected between the hours of 8 AM, February 10 and 8 AM February 11, 1953. The initial pH of the waste stream was 6.25 and the hardness 158 ppm as $CaCO_3$. At concentrations corresponding to variable flow volumes, the observed pH and hardness values were as follows:

Stream Flow (gpm	69	139	208	278	347	416	486	556	694	694
" (mgd	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Observed pH	6.45	6.50	6.45	6.55	6.55	6.50	6.56	6.60	6.65	6.85
Observed Total Hardness* - ppm	2560	1350	870	700	650	570	510	490	490	401
Net Increase in Hardness - ppm	2402	1192	712	542	492	412	352	332	332	243

*As $CaCO_3$

From this table it will be noted that the pH was increased from 6.25 to 6.45 - 6.85 and the hardness from 158 to 401 - 2560. These values are plotted in the accompanying graph. All materials were completely soluble even at the highest concentrations. However, when the pH was increased to 10.0 to 10.7 by adding from 0.1 to 1.0 ml of concentrated NaOH, considerable amounts of rapid-settling precipitates were produced. An examination of the hardness in the container containing 2560 ppm hardness showed that the hardness was reduced to 1230 ppm. The sludge volume amounted to about 50 ml per 500 ml of initial dilute waste volume. This reprecipitation might be viewed with some concern inasmuch as the pH of the settling basin may vary over exceedingly wide ranges and precipitation might take place at certain times. This precipitate, if accumulated because of the sluggish flows in White Oak Creek, and then redissolved, as a result of the discharge of acid wastes, could possibly result in considerably higher concentrations of these respective chemical compounds. The deposition of sludges or precipitates, when the pH becomes more alkaline as noted above, may result in the formation of sludge banks of considerable magnitude since potentially large amounts of waste materials are being discharged (a little over 6 tons of chemicals exclusive of water) daily. The addition of this large quantity of salts to the water of White Oak Creek will increase the total solids concentration by approximately 1225 ppm, at the least, when the flow in the Creek amounts to about 500 gpm.

Further dilution (possibly up to 1,000 times, if complete mixing is assumed), will be provided following discharge into the Clinch River. The actual concentrations that will result will be dependent entirely upon what took place in White Oak Creek and White Oak Lake.

Since PDA seems to be quite critical from a possible toxicity standpoint, concentrations which are considered toxic are shown crosshatched in the attached graph. Concentrations above 5,000 ppm NaCl should also be avoided if possible, as well as concentrations of Na_2SO_4 above 7,106 ppm. Except for PDA whose concentration will reach the tentative critical value of 30 ppm at a flow of 500 gpm, toxic or critical concentrations of NaCl and Na_2SO_4 will not be reached until the flow volume is reduced to 40 and 28 gpm, respectively.

[redacted]

It would be desirable to develop a method - preferably a method that is rapid - for the determination of the actual concentration of PDA in the waste stream. This test should be sufficiently sensitive to measure concentrations of PDA as low as 1 ppm.

Certain control tests will have to be specified to insure that the critical concentrations of these chemical constituents are not exceeded, but these will not be included herein. Once approval for the process has been obtained, this matter can be reopened at that time.

It is presumed that before any materials are discharged into the White Oak Creek system, these discharges will be cleared with the Health Physics Division to ascertain that no possible interference with existing studies being made of the White Oak Creek drainage system and/or its ecology can take place.

[redacted]
Conrad P. Straub

CPS/br

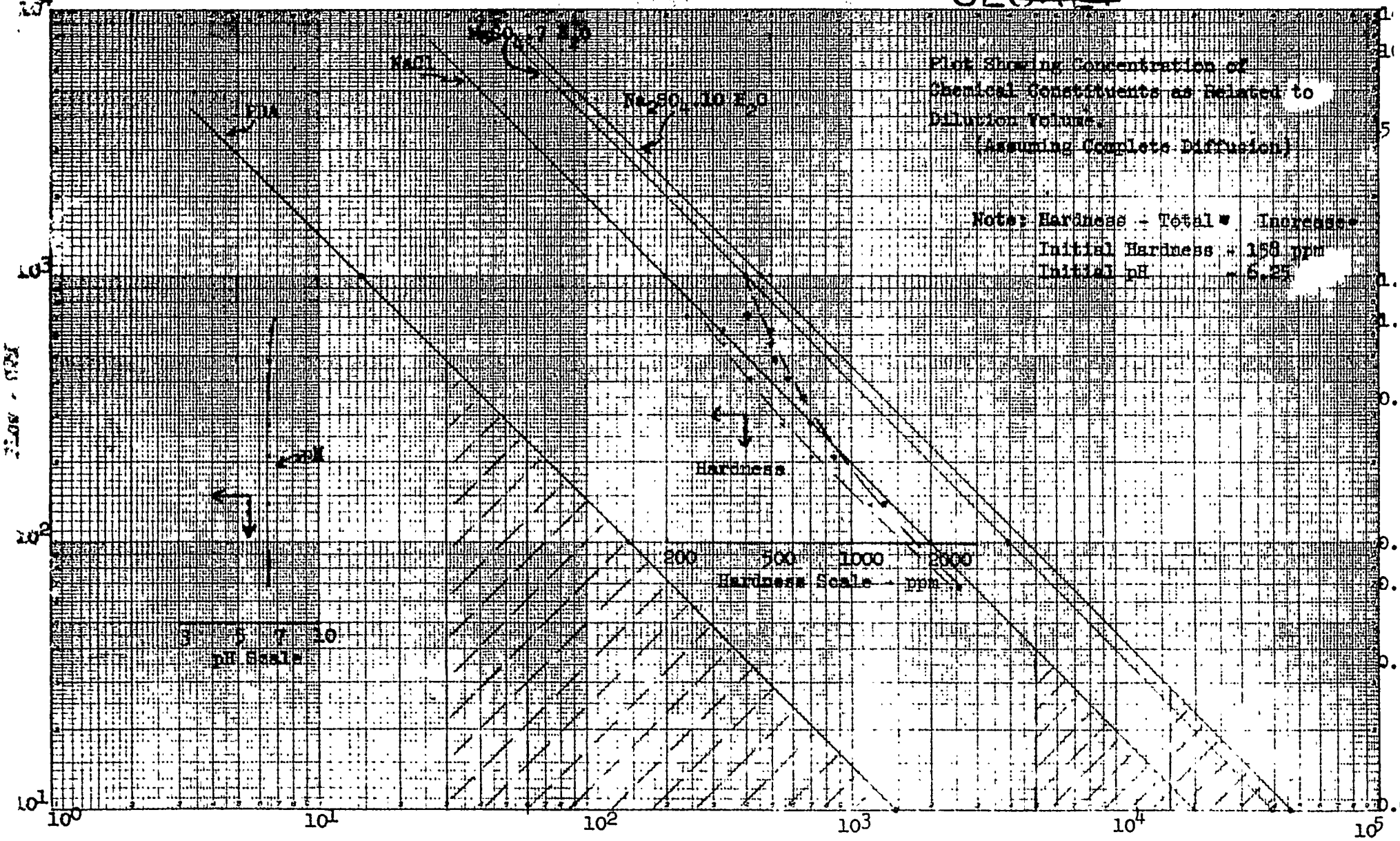
cc: W. J. Lilley
R. J. Morton - O. R. Placak
L. A. Krumholz
C. P. Straub
H. P. Milford
F. L. Culler
F. L. Steahly

[redacted]

[redacted]

[redacted]

[redacted]



Concentration of given chemical in ppm (mg/l) under given flow conditions.

[redacted]

Author: Jennifer Lamb at MH-Alameda
Date: 7/11/96 11:42 AM
Priority: Urgent
TO: Susan Flack
Subject: Re: REVISED Request for Inmagic Documents
---------- Message Contents ----------

Susan,

I checked on these documents our records indicated that you checked out document numbers 1581, 1258, and 1451 last March/April. Do you still have those documents...or did you send them back and I put them somewhere safe but didn't refile them. I am sending documents 2788 and 2802. My notes say that I sent document 2732 to Shonka. I sent Sylvia an email requesting the document. Hope that takes care of everything.

Jennifer

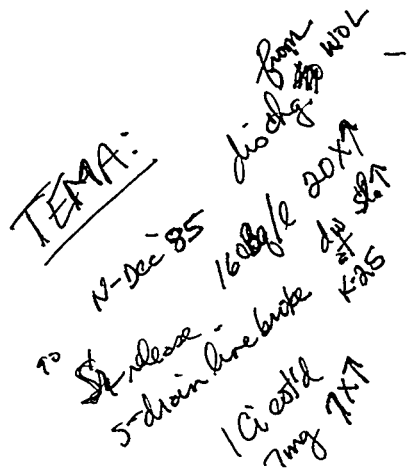
Jenny K/Brian-

Could you send me:

✓ *** 1581 Orex
✓ *** 2788 Thorex
✓ 2732 (K25 Hg recovery facility) ALA
✓ 2802 " "
1258 waste disposal monthly copyloc?
1451 " " ALA

CLEVELAND document: 2696 waste disposal monthly
Brian, does this type of report have the curies released over WOD like the ones from the 60s? As before, I just need that one table.

THX!!!
Susan



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DRAFT

RGP # 112

00533

ornl

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

HISTORICAL CHEMICAL RELEASE REPORT

FOR

OAK RIDGE NATIONAL LABORATORY

Susan,
I ran across this today. You may already have it but I thought I'd pass it on.
JKL

DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

ENVIRONMENTAL AND OCCUPATIONAL SAFETY DIVISON

OAK RIDGE NATIONAL LABORATORY

May 1986

NOTICE:

Publicly Releasable

This document has received the necessary patent and technical information reviews and can be distributed without limitation.

final patent nformation is ; to be given ordance with

DOC # 112

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

DRAFT

CHEMICAL RELEASE DATA FORM

Chemical Name: Mercury
Uses: Lamps, batteries, gauges, instruments, chemical laboratory uses
Solid _____ Liquid __X__ Gas _____.
Listed as Toxic: Yes __X__ No _____.

Status of Environmental Compliance (Past and Present):

At present all discharges conform to existing ORNL permit conditions. The ORNL NPDES permit (1975-1980) did not contain discharge limitations for any of the listed chemicals. The present NPDES permit (1986-1990) lists only chloroform, PCBs and trichlorethylene and these are monitoring only requirements. The primary reason for this is that existing data do not indicate that the chemicals are being released via surface water discharges. If after the mandatory year's monitoring, certain of these appear in sufficient quantity then limitations may be imposed. The organic compounds, benzene, chloroform, methylene chloride, tetrachloroethylene, and trichloroethylene appear with limits for the Nonradiological Wastewater Treatment Plant (X12), but this facility is not scheduled to be completed until 1990 and thus the limitations are not effective until that time.

Known or Suspected Public Health Impacts:

- No known or suspected public health impacts.

Known or Suspected Environmental Impacts:

There were twelve cases of recorded mercury spills at ORNL ranging from trace amounts to 0.1 kg (0.22 lb) between 1980 and 1985. There were no known environmental impacts from these spills.

There have been occasions at ORNL when pockets of mercury were discovered at pipes or under tiles. These small quantities are attributed to the processes which were undertaken at ORNL to support the Y-12 thermonuclear weapons program. These operations took place in the 1950s and 1960s at Bldgs. 4501, 3503, and 3592. Though there is not an accurate measure of the mercury loss at ORNL, operating personnel have estimated losses of 907 - 1361 kg (2000-3000 lb) due to spills and leakage.

In a recent study, soil samples collected around Bldg. 4501 contained mercury concentrations ranging from 0.05 to 4.4 ppm. However, one sample was as high as 465 ppm. Soil samples near Bldg. 3503 contained mercury concentrations ranging from 0.8 to 25 ppm and near Bldg. 3592 the samples ranged from 4.1 to 320 ppm.

Known or Suspected Environmental Impacts: (cont.)

Though there were individual fish samples with higher concentrations, all average values of mercury concentrations in Clinch River fish were below the Food and Drug Administration action level of 100 ng/g.

Mercury concentrations in water collected at White Oak Dam, White Oak Creek, and Melton Hill Dam were all higher than the Tennessee stream criteria. (Source: Environmental Monitoring Report, ORNL-6209). not in 1979, 80 or 81

1984 Rep. No. 955

Level and Type of Worker Protection:

Specific use, conditions, quantities, and other factors determine the level and type of worker protection. Standard measures for protection against this material include one or more of the following: (1) adequate ventilation, (2) protective clothing, (3) chemical goggles, (4) face shield, and (5) proper respiratory protection.

Source of Chemical Usage Information:

Information taken from the Annual Toxic Chemical Usage by ORNL Department - Report 3063, ORNL Hazardous Materials Usage Reconciliation - Report 7010, and purchase requisitions with ORNL account numbers for 1980-1985.

Source of Chemical Distribution Information/Accuracy:

- Hazardous waste disposal records.

CARTRIDGE T-12 PLANT INFORMATION CONTROL FORM RP

DOCUMENT DESCRIPTION (Completed By Requesting Division)

Document No	Author's Telephone No.	Acct. No	Date of Request
Y/HG-0549	6-0263		

Unclassified Title: Survey Questionnaire: Mercury usage + flow in U.S. Government Installations

Author(s): Requestor: Steve Wiley for ChemRisk Phase II M-458

TYPE ☐ Formal Report ☐ Informal Report ☐ Progress/Status Report ☐ Co-Op Report ☐ Thesis/Term Paper

☐ Oral Presentation (identify meeting, sponsor, location, date) _____

☐ Journal Article (Identify Journal): _____

☐ Other (Specify): _____

Document will be published in proceedings ☐ No ☐ Yes

Document will be distributed at meeting ☐ No ☐ Yes

Document has patent or invention significance ☐ No ☐ Yes (Identify) _____

Document has been previously released ☐ No ☐ Yes (Reference) (YMS. 5.25.90 P 6/8/90

DIVISION REVIEW AND APPROVAL (Completed By Requesting Division)

TECHNICAL CLASSIFICATION REVIEW (Divisional Classification Representative)

Title(s) Unclassified Abstract —

DOCUMENT Level Unclassified Category —

M.F. Quigley 11 Sept 1995
Signature Date

Y-12 Plant Classification Office

DOCUMENT REQUEST APPROVED (Division or Department)

[signature] 9/15/95
Signature Date

Signature Date

THE REMAINDER OF THIS FORM TO BE COMPLETED BY THE TECHNICAL INFORMATION OFFICE

DISTRIBUTION

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External Distribution

TID-4500 Category _____ or _____ Copies to OSTI

ANNOUNCED IN: ERA Atomindex (Available from NTIS)

M-3679 Category _____

ANNOUNCE IN. ☐ AWDR (Available from OSTI) ☐ ANCR

Distribution:	UCN-7721B	DOE F-1332.15	Document
Y-12 Central Files	Y-12 RC	Y-12 RC	Y-12 RC
TIO File			

Distribution Remarks: Unlimited (ChemRisk)

APPROVAL AND RELEASE

Date Received | Date Initiated 9/15/95

[2] CLASSIFICATIONS

Title(s) U Abstract NA

DOCUMENT:

Level U Category —

Weapons Data — Sigma _____

R.C. Fraser 9/18/95
Y-12 Classification Office Date

☐ _____ Editor Date

[3] Waived / P. McKenney Patent Office Date

☐ _____ Date

☐ _____ Date

APPROVED FOR: ☐ Declassification ☐ Release subject to use of the following admonitory markings and conditions:

☐ Disclaimer ☐ Copyright ☐ Patent Caution ☐ Other

P.R. McKenney 9/22/95
Technical Information Office Date

Conditions/Remarks

UCN-7721B
2 1-66)

OAK RIDGE Y-12 PLANT INFORMATION CONTROL FORM

GRL 5/31/90

DOCUMENT DESCRIPTION (Completed By Requesting Division)

Document No.	Author's Telephone No.	Acct. No.	Date of Request
MS 5-25-90 P	4-7593	2366-001	5/25/90

Unclassified Title: SURVEY QUESTIONNAIRE : MERCURY USAGE AND FLOW IN U.S. GOVERNMENT INSTALLATIONS M-458

Author(s): FULKENSON, W

TYPE: ☐ Formal Report ☐ Informal Report ☐ Progress/Status Report ☐ Co-Op Report ☐ Thesis/Term Paper

☐ Oral Presentation (identify meeting, sponsor, location, date):

☐ Journal Article (Identify Journal):

☒ Other (Specify): JUNE 7, 1992 LETTER TO PR VANSICKLE

Document will be published in proceedings ☒ No ☐ Yes

Document will be distributed at meeting ☒ No ☐ Yes

Document has patent or invention significance ☒ No ☐ Yes (Identify)

Document has been previously released ☒ No ☐ Yes (Reference)

DIVISION REVIEW AND APPROVAL (Completed By Requesting Division)

TECHNICAL CLASSIFICATION REVIEW (Divisional Classification Representative)

Title(s): UNC Abstract: NA

DOCUMENT: Level UNC Category NA

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Weapons Data Sigma

J R Byrd 6-4-90
Y-12 Classification Office Date

☒ G. Keith 6-4-90
Patent Office Date

☒ J L Langford 6-1-90
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☒ D E Wood 6/5/90
Other NB Legal review Wood Date

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GRL 6/8/90

4/HG-0549

QUESTIONNAIRE: MERCURY USAGE AND FLOW IN U.S. GOVERNMENT INSTALLATIONS

Form filled in by: Date: March 24, 1972

Name Walter E. Clark

Organization Oak Ridge National Laboratory

Address P. O. Box "X"

City, State, Zip Code Oak Ridge, Tenn. 37830

Telephone (include area code) (615) 483-8611, Ext. 3-6063

FTS Telephone (if different from above (615) 483-6063

1. Annual Mercury Usage (Please circle either) (Calendar year 1971) Fiscal year 1971
(Please enter "G" at the extreme right by each item obtained through GSA.)

	Compound (lb)	Conversion Factor to Metal	Metal (lb)	GSA
a. Metallic mercury	136.0	1.000	136.0	
b. Mercury compounds				
Mercuric acetate [$Hg(C_2H_3O_2)_2$]	0	0.629	0	
Mercuric chloride ("bichloride" or "corrosive sublimate," $HgCl_2$)	0	0.739	0	
Mercuric iodide (HgI_2)	0	0.441	0	
Mercuric nitrate [$Hg(NO_3)_2 \cdot 1/2\ H_2O$]	16.25	0.585	9.5	
Mercuric oxide (HgO)	0	0.926	0	
Mercuric sulfide (HgS)	0	0.862	0	
Mercuric sulfate ($HgSO_4$)	0	0.676	0	
Mercurous chloride ("calomel," Hg_2Cl_2)	1	0.850	0.9	
Mercurous nitrate ($HgNO_3 \cdot H_2O$)	4	0.715	2.9	
Mercurous sulfate (Hg_2SO_4)	0	0.807	0	
Sodium amalgam, %	0		0	

d. Is your solid waste disposed of

In landfill	Yes (✓)	No ( )
By incinerator	Yes ( )	No (✓)
Other (please specify)	Yes ( )	No (✓)

_____

_____

e. If your solid waste is disposed of other than by landfill, are mercury-containing items segregated for landfill? Yes ( ) No ( )

f. Do you remove mercury from your liquid effluents before discharge to the sewer? Yes ( ) No (✓)*

3. g. Please give as much information as possible (on separate sheets) concerning the composition of effluent streams responsible for mercury loss from your operation. What are your recommended procedures for minimizing mercury loss from each source? Flowsheets for each process with approximate mass balances for the mercury would be especially helpful.

Summary of Mercury Usage, Lb

	1971
From metal and chemicals (Questions 1a, 1b)	149.3
From manufactured items (Question 1c)	135.2
Total pounds mercury	284.5

*See 3g (~~attached sheet~~ above)

Question 3g

Minimum mercury discharge to the sewer can be considered to be equal to the usage of mercury chemicals, i.e., 13.3 lb of mercury (calculated as metal) per year. At ORNL non-radioactive process waste water is discharged to a storm sewer which, in turn, discharges to a natural stream to which the effluent from the low-level radioactive waste treatment plant and the sanitary sewage treatment plant also discharge. The stream is monitored for mercury regularly at several points. On a few occasions minute traces of mercury have been detected. It is not clear from the results whether or not these represented current discharges from the plant or dislodgement of sediment containing mercury from earlier discharges.

High and intermediate-level radioactive wastes are stored in underground tanks. Low-level radioactive waste is discharged to a settling pond, the effluent from which goes through a lime-soda precipitation step before discharge to the stream. Sludge from this plant has in the past been disposed of by hydrofracture into a local shale formation along with intermediate-level waste mixed with concrete grout. At present intermediate-level waste is being retained in tanks pending a decision on final disposition. Meanwhile, any mercury in this waste is contained along with other constituents.

All ORNL solid waste is sent to a sanitary landfill operated for the three local AEC contractor-operated plants by contractor personnel. Fluorescent bulbs and non-recyclable batteries are included in the waste buried there. No private or municipal waste is handled at the landfill and there is no incineration or open burning.

Mercury batteries are collected for recycle. The reprocessing is done by an outside firm on a bid basis.

Dirty mercury, uncontaminated by radioisotopes, is cleaned by nitric acid treatment and returned to use. Mercury dissolved in the nitric acid effluent is removed by displacement with aluminum before the effluent is discharged. The operation is normally handled on an occasional small batch basis by one man in the Analytical Chemistry Division. In 1971, he processed about 1800 lb of mercury for ORNL, plus some for the other plants. Mercury which is used in radioactively hot operations (principally in coulometers) is redistilled and reused in the same operations.

There are presently no large-scale uses of mercury at ORNL nor any routine generation of large volumes of low-level wastes (e.g., from COD tests). Should such wastes be generated in the future, we propose to remove the mercury either by displacement with an active metal or as sulfide by the procedure described by Dean, Williams, and Wise of EPA in *Environmental Science and Technology* 5, 1044-5 (1971). The amounts and nature of the waste generated will determine which procedure is most practical.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE CORPORATION
NUCLEAR DIVISION

1982 DEC -9 AM 11:57

POST OFFICE BOX X
OAK RIDGE, TENNESSEE 37830

December 3, 1982

Mr. J. F. Wing, Chief
Environmental Protection Branch
Department of Energy
Post Office Box E
Oak Ridge, Tennessee 37830

WOD 1979
0.4 ppm MAX
(TN Stream 5ppm)
1980 LOD 1 ppm

Dear Mr. Wing:

FOI REQUEST FOR DATA - MERCURY IN WATER

As requested in your letter of November 30, 1982, enclosed are the data on mercury in water for 1979, 1980, and 1981. If there are any questions or any additional data is needed, feel free to let me know.

Sincerely,

T. W. Oakes

T. W. Oakes,
ORNL Environmental Coordinator

Enc.

TWO:WFO:aw

cc: E. Aebischer
J. A. Auxier
R. G. Jordan
C. R. Richmond
K. W. Sommerfeld

Table 4.4.6 Chemical Water Quality Data
White Oak Dam - 1979

Substance	Number of Samples	Concentration (µg/l) ppm				
		Maximum	Minimum	Average	Std.[a]	% Std.
Cr	11	3.8	1.3	2.5 ± 0.5	50	5
Zn	11	43	2.4	13 ± 8	100	13
NO_3(N)	11	4,300	240	2700 ± 800	10,000	27
Hg	12	.37	.001	0.1 ± 0.06	5	2

[a]Tennessee Stream Guidelines. 0.00037 ppt

Table 4.4.7 Chemical Water Quality Data
Melton Hill Dam - 1979

Substance	Number of Samples	Concentration (µg/l)				% Std.
		Maximum	Minimum	Average	Std.[a]	
Cr	11	0.6	0.05	0.05 ± 0.2	50	1
Zn	11	2.0	0.1	0.7 ± 0.4	100	0.7
NO_3(N)	11	2,460	7	360 ± 430	10,000	3.6
Hg	12	0.09	0.001	0.03 ± 0.02	5	0.6

[a]Tennessee Stream Guidelines.

Table 4.4.6 Chemical Water Quality Data
White Oak Dam - 1980

Substance	No. of Samples	Concentration (mg/ℓ) ppt Maximum	Minimum	Average	Std.[a]	% Std.
Cr	10	< 0.01	< 0.01	< 0.01	0.05	< 20
Zn	10	< 0.02	< 0.02	< 0.02	0.1	< 20
$NO_3(N)$	10	9.8	0.01	4.6 ± 2.2	10	46
Hg	12	< 0.001	< 0.001	< 0.001	0.005	< 20

[a]Tennessee Stream Guidelines.

1ppm L.O.D.

5ppm

Table 4.4.7 Chemical Water Quality Data
Melton Hill Dam - 1980

Substance	No. of Samples	Concentration (mg/ℓ) Maximum	Minimum	Average	Std.[a]	% Std.
Cr	10	< 0.01	< 0.01	< 0.01	0.05	< 20
Zn	10	< 0.02	< 0.02	< 0.02	0.1	< 20
NO_3(N)	10	2.2	0.1	0.55 ± 0.5	10	< 6
Hg	11	< 0.001	< 0.001	< 0.001	0.005	< 20

[a]Tennessee Stream Guidelines.

Table 15
CHEMICAL WATER QUALITY DATA - WHITE OAK DAM
1981

SUBSTANCE	NUMBER OF SAMPLES	CONCENTRATION, mg/L (ppt)				% STD.
		MAXIMUM	MINIMUM	AVERAGE	STD.[a]	
Cr	4	< 0.01	< 0.01	< 0.01	0.05	< 20
Zn	5	< 0.02	< 0.02	< 0.02	0.1	< 20
$NO_3(N)$	5	8.3	3.6	6.1 ± 1.7	10	61
Hg	5	0.002	< 0.001	< 0.001	0.005	< 20

[a]Tennessee Steam Guidelines.

Table 16
CHEMICAL WATER QUALITY DATA - MELTON HILL DAM
(Location C-2, Figure 3)
1981

SUBSTANCE	NUMBER OF SAMPLES	CONCENTRATION, mg/L				% STD.
		MAXIMUM	MINIMUM	AVERAGE	STD.[a]	
Cr	4	< 0.01	< 0.01	< 0.01	0.05	< 20
Zn	5	< 0.02	< 0.02	< 0.02	0.1	< 20
$NO_3(N)$	5	0.98	0.63	0.86 ± 0.1	10	8.6
Hg	6	< 0.001	< 0.001	< 0.001	0.005	< 20

[a]Tennessee Steam Guidelines.

APPROVAL FOR RELEASE

Document: # Unnumbered 1-page ltr, TW Oakes to JF Wing ~~(DOE-ORO), FOI REQUEST FOR DATA~~ Date _____;

Title/Subject MERCURY IN WATER; and ~~6-page attachment~~

Approval for unrestricted release of this document is authorized by the Oak Ridge K-25 Site Classification and Information Control Office, Martin Marietta Energy Systems, Inc., PO Box 2003, Oak Ridge, TN 37831-7307.

Irwin S. Smith

K-25 Classification & Information Control Officer

1/29/93

Date

X-10
MHDam
WODam

1979,80,81

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Title of requested document FOI Request for Data - Mercury in Water

Document Number S02405, S02406, S02407

Access Number of Document _____ Date of Document December 1982

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Derivative Classifier T.G. Jordan Phone 41645

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Document number S02405, S02406, S02407 Pages _____

Document title FOI Request for Data - Monitoring Well

Author(s) (indicate other divisions or organizations, if applicable) _____

Document type (See Doc. Prep. Guide, Chs. 1 and 2, for definitions of document types):

☐ Formal Report ☐ Progress Report ☐ Informal R&D Report ☐ Abstract ☐ Drawing

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As Client Risk.

Technical Information Officer Signature Quinn S. Spirit (43) Date 1/29/93

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JCN-87 BACK

McLAREN/HART ALAMEDA OFFICE

This is a facsimile from McLaren/Hart Environmental Engineering Corporation, 1135 Atlantic Avenue, Alameda, CA 94501. Our dedicated FAX number is (510) 521-1547. Our telephone number is (510) 521-5200.

Attention: Susan Flack

I am sending 5 **page(s), including this cover sheet.**

Date: 11/28/95 **Time Out:** _____

FAX Number Called: (303) 939-8318 **Job/Task:** _____

MESSAGE: Susan,

These are excerpts from some Environmental Committee meetings that I pulled out. I am entering the whole set of documents (meeting minutes 1971-1977) in the database.

CEP Compliance and Environmental Policy Dept.

R. Jordan's copies

Sincerely,

J. Lamb (510) 748-5641

Person Transmitting Copy *Direct Telephone Number*

McLaren Hart

INSERT TABLE 3-1

INTRA-LABORATORY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY

From: JCC-ND Environmental Monitoring and Protection Committee meeting 7/10/74

POLLUTION CONTROL PROJECTS - ORNL

1. Two ponds for controlling pH in White Oak Creek.

   This project, for $90,000, is awaiting AEC approval of funds. The money was promised by FY1975.

2. Chromates

   The operation of the 4500 Area cooling tower and most of the small cooling towers has been changed to use phosphonates instead of chromates. The HFIR cooling tower blowdown has been reduced by 70% by using the lime-soda-ash treatment. The chemistry of the HFIR cooling tower process is being modified in an effort to completely eliminate the blowdown.

   The only area where the chromate discharge is significant and nothing has been done is at the ORR and BSR cooling towers. The work is being held up here to see what the outcome will be on the electrolylic process at Y-12.

3. Bulk Chemical Storage

   Work orders have been issued to modify drainage at all tanks where potential releases of significant amounts of chemicals are possible. Where the modifications were not practical, the tanks were taken out of service.

4. Oil Pollution

   (a) SPCC plan written. Engineers are now working on devising a method for anchoring sorbent booms at White Oak Dam.

   (b) There are only two above-ground tanks that require diking; one is the 70,000-gal. tank at the Steam Plant and the other is a 5,000-gal. tank at the MSRE. The existing dike around the tank at the Steam Plant needs minor modification to conform with the SPCC procedure. The 5,000-gal. tank at the MSRE is being removed from service.

TABLE 2-6

ESTIMATION OF RELATIVE IMPORTANCE OF EXPOSURE PATHWAYS

Pathway	Dose (a)	Toxicity Criterion (b)	Hazard Index	Percent of Largest Pathway
Surface Water Pathways: Inorganic Mercury (0.026 mg/L)				
Water to Humans (Incidental Ingestion)	9.3×10^{-7}	3.0×10^{-4}	0.0031	64%
Water to Livestock/Game (Beef) to Humans (Ingestion)	1.4×10^{-6}	3.0×10^{-4}	0.0048	100%
Water to Dairy Cattle (Milk) to Humans (Ingestion)	2.2×10^{-8}	3.0×10^{-4}	0.000073	2%
Water to Humans (Recreational- Dermal Contact)	3.2×10^{-8}	3.0×10^{-4}	0.00011	2%
		Total Hazard (Surface Water)	**0.0081**	
Fish Pathway: Methyl Mercury (2.7 mg/kg)				
Fish to Humans (Ingestion)	1.0×10^{-3}	1.0×10^{-4}	10	100%
		Total Hazard (Fish)	**7.8**	

a All values represent average daily doses in mg/kg-day, with the exception of the Air to Humans (Inhalation) pathway. The value for this pathway represents an average daily air concentration in mg/m^3.

b All values represent Reference Doses (RfDs) in mg/kg-day, with the exception of the value for the Air to Humans (Inhalation) pathway. The value for this pathway represents a Reference Concentration (RfC) in mg/m^3.

5. Sewage Plant Discharge

The secondary sewage treatment ponds are now being constructed and should be in operation late this calendar year. The operation of the ponds should eliminate the low dissolved oxygen in White Oak Creek.

Susan

6. Mercury in White Oak Creek

We occasionally find mercury in excess of 0.005 ppm in White Oak Creek although we have not found it above that level at White Oak Dam in the last 1-1/2 years since we started analyzing for mercury. An investigation has shown that the source of mercury is the 4500 Area where metallic mercury has been found under the concrete basement floor. The job for doing something about eliminating the discharge has been recently assigned to the Chemical Technology Division.

7. PCB

Dan Nelson is getting ready to sample the river upstream from ORNL and White Oak Lake. K-25 sampling finished.

Procedure for handling PCB at ORNL has been written but needs modification as we have discussed over the phone.

8. Process Waste Treatment Plant

Construction is in progress and should be completed late this year. The plant is expected to remove 40% of the strontium activity being released to the river.

9. Burial Ground Study

The Environmental Sciences Division is studying means to reduce the release of activity from the burial grounds to the creek. A total of $150,000 was appropriated for this study for FY1974, and proposals for future years are being prepared.

INSERT FIGURE 3-3

UCC-ND ENVIRONMENTAL MONITORING AND PROTECTION COMMITTEE MEETING

March 4, 1976

The UCC-ND Environmental Monitoring and Protection Committee convened on March 4, 1976, 9:00 a.m., in Oak Ridge. Those in attendance were H. H. Abee, R. C. Baker, M. C. Conrad, D. G. Jacobs, R. G. Jordan, J. C. Little, M. E. Mitchell, T. W. Oakes, M. Sanders, and I. G. Speas. J. K. Alexander and J. F. Wing, ERDA Environmental Protection Branch, were guests at the meeting.

ERDA Operating Limits for Quantities or Concentrations of Radioactive Materials Released

H. H. Abee stated that during last year's ERDA Environmental Management Appraisal of ORGDP, the establishment of operating limits for releases of radioactive materials was mentioned by Mr. H. W. Hibbitts of ORO. The subject of operating limits is set forth in Manual Chapter 0511, Radioactive Waste Management, which states ..."Managers of Field Offices: d. maintain suitable approval control over key waste management decisions of operating contractors, such as the establishment or major modification of: (1) operating limits for quantities or concentrations of radioactive materials released to the environment." While this activity normally would be a function of the ORO Waste Management Branch, Mr. Hibbitts stated that Waste Management has asked the Environmental Protection Branch to implement this requirement.

Mr. Abee noted that, while this subject was not discussed in the ORGDP appraisal report, a request for establishment of operating limits could be anticipated some time in the future. Later discussions with Mr. Hibbitts indicated that the Environmental Protection Branch interprets operating limits to be administrative reporting limits which are set at some point above the normally experienced average discharge levels. Mr. Wing concurred with this interpretation and expressed ORO's need for more rapid notification of above normal release levels than is currently available through normal reporting mechanisms.

Mr. Abee requested that each installation examine past releases, prepare suggested administrative reporting limits for radioactive releases, and submit suggested limits to the UCC-ND Safety and Environmental Protection Office for review and concurrence with the ORO Environmental Protection Branch. A range of 2 to 10 times the average release level, depending upon the hazard of the material released and the normal fluctuations experience for a given time period, was suggested as a criterion for setting administrative reporting levels.

Quality Assurance Documentation Status

M. Sanders reported that a quality assurance plan has been prepared for the Y-12 monitoring program. The plan was reviewed by Y-12 Quality Assurance personnel, audited by ORO Quality Assurance auditors, approved, and

INSERT TABLE 3-5

Pollution Control Project Status

Pollution control projects currently in progress at each of the four installations were discussed. Summaries of the pollution control project status are included as attachments.

Items of Note

M. C. Conrad reported that a number of new static capacitors which were installed in the electrical switch yards at Paducah have failed. Several capacitors ruptured upon failure and sprayed pyranol (PCB) over an approximate 20 ft. diameter area. Cleanup, using sorbent material and other techniques, has been attempted. Considerable difficulty has been experienced with cleanup due to the fine nature of the spray from the rupture.

Mr. Conrad stated that Paducah is now using flow weighted averaging for effluent parameters and, with concurrence from ORO Environmental Protection Branch, is now sampling sewer plant effluent for BOD_5 after chlorination.

Susan

M. E. Mitchell raised the question of the proper disposal method for mercury vapor lamps. The suggested procedure was to collect the lamps, break them under water in a 55 gallon drum, allow the mercury to accumulate in the bottom of the drum, and collect the mercury for redistillation and reuse. Disposal of mercury vapor lamps in the sanitary land fill should be discontinued.

Mr. Mitchell requested guidance from the ORO Environmental Protection Branch representatives on the expediency and extent of biota sampling needed in Poplar Creek with regard to potential mercury contamination from mercury contained in the sediments. Mr. Wing stated that the Environmental Protection Branch would consider the problem and provide guidance on the scope of the sampling program in a few weeks.

H. H. Abee distributed copies of ERDA budget assumptions for Environmental Control, OSHA, and Energy Conservation planning, and copies of information from the Environment Reporter concerning amendments to the Clean Air Act which relate to federal facilities.

Meeting Schedule

The next meeting of the Committee will be held in Paducah on July 14, 1976.

R. G. Jordan

RGJ:HHA:cm

Attachments

ChemRisk/Shonka Research Associates, Inc., Document Request Form

(This section to be completed by subcontractor requesting document)

J. Lamb / K-25 ER

Requestor / Document Center (is requested to provide the following document)

Date of request 10/23/96 Expected receipt of document 11/23/96

Document number ORNL/M-2375 Date of document 7/5/83

Title and author (if document is unnumbered)

(This section to be completed by Document Center)

Date request received 10/28/96

Date submitted to ADC NA

Date submitted to HSA Coordinator 10/28/96

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Date submitted to CICO N/A

Date received from CICO Previously Released 10/21/92

Date submitted to ChemRisk/Shonka and DOE 10-30-96

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ORNL/M-2375

July 5, 1983

Mr. J. F. Wing
Office of Assistant Manager
for Safety and Environment
Department of Energy
Oak Ridge Operations
Post Office Box E
Oak Ridge, Tennessee 37830

Dear Mr. Wing:

MERCURY CONCENTRATIONS IN SOIL SAMPLES COLLECTED AROUND BUILDINGS 4501, 4505, 4507, AND FROM THE BANK OF FIFTH CREEK

Reference: T. W. Oakes to J. F. Wing, "Mercury in Soil and Sediment at ORNL," dated June 9, 1983

As requested by G. Marciante, we are enclosing the data on soil core samples taken in the area of Buildings 4501, 4505, 4507, and Fifth Creek. Mercury data on White Oak Creek sediment and soil samples near Buildings 3503 and 3592 were forwarded to your office earlier (reference correspondence). The five soil samples with the highest mercury concentration were also analyzed per the RCRA EP toxic procedure and the results are listed in the attached table.

A map showing the sample points has been included. Further assessments are underway to examine possible environmental impacts.

Sincerely,

T. W. Oakes

T. W. Oakes
ORNL Environmental Coordinator

TWO:BME:ac

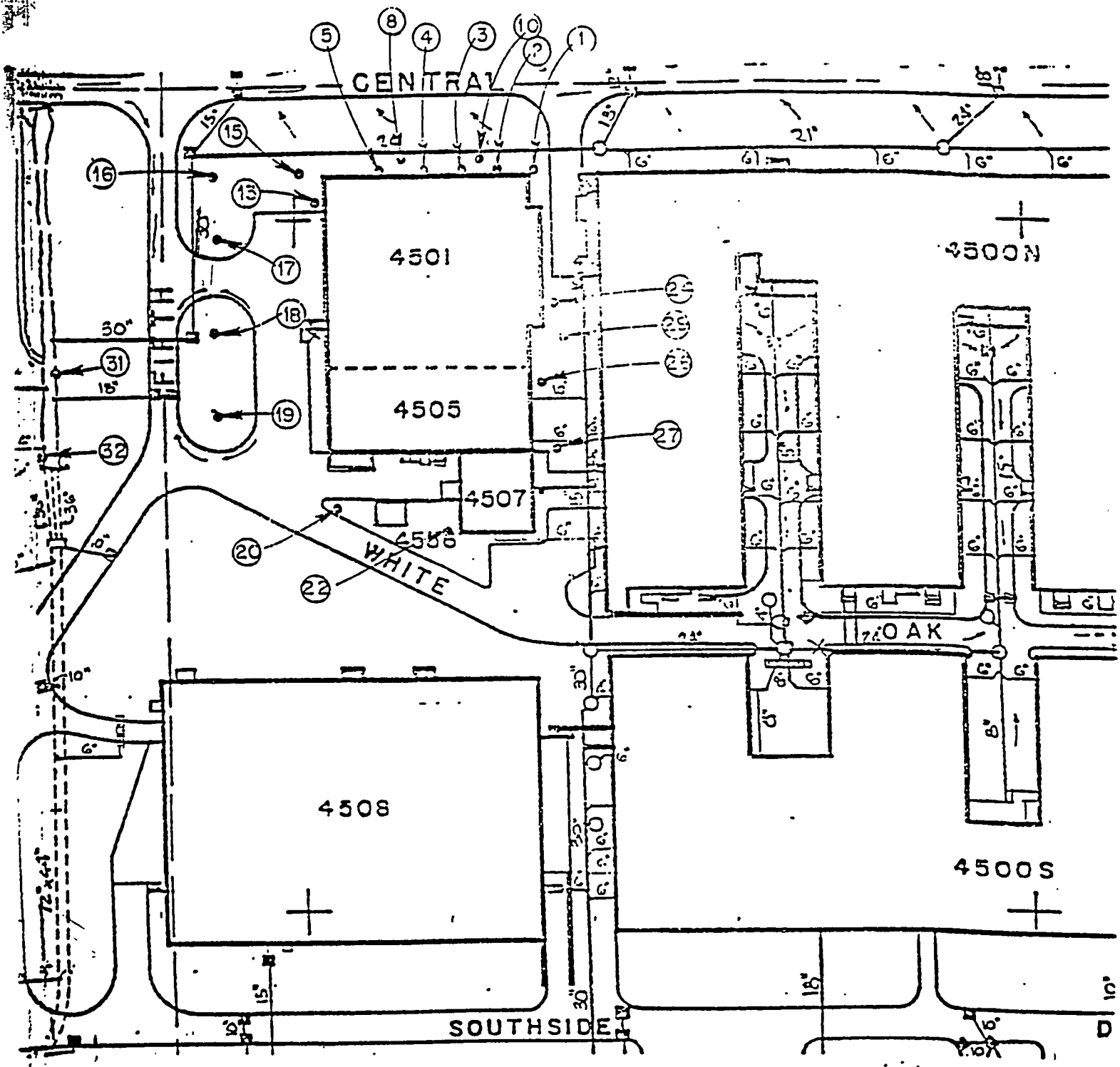
Attachments

cc/att: R. L. Egli (DOE)
D. E. Ferguson
R. G. Jordan
J. A. Lenhard (DOE)
D. C. Parzyck
C. R. Richmond
K. W. Sommerfeld (2)
W. J. Wilcox
File - RC

SUMMARY OF MERCURY ANALYSES IN SOIL SAMPLES - BUILDINGS 4501, 4505, AND 4507

Sample Area	Mercury Concentration (µg/g dry wt)	RCRA EP Toxic Analysis Mercury (mg/l)
4501-1	0.29	
4501-2	0.25	
4501-3	0.32	
4501-4	0.23	
4501-5	0.70	
4501-8	0.44	
4501-10	0.29	
4501-13	4.4	3
4501-15	2.3	<2
4501-16	1.1	
4501-17	0.12	
4501-18	0.38	
4501-19	1.4	
4501-20	0.05	
4501-22	0.33	
4501-24	0.70	
4501-25	13	
4501-27	3.8	<2
4501-29	1.4	
Bank of Fifth Creek-31	465	66
Bank of Fifth Creek-32	3.5	<2

009049


CENTRAL
4501
4505
4507
4508
WHITE
OAK
SOUTHSIDE
4500N
4500S
FIFTH

4501 Soil 1983	mean +/-SD	3592 Soil	mean +/-SD	3503 Soil	mean +/-SD
ppm dry					
0.29	**23.8**	4.1	**111.0**	25	**8.9**
0.25	101.1	8.8	181.0	3.2	11.0
0.32		320		6.5	
0.23				0.8	
0.7					
0.44					
0.29					
4.4					
2.3					
1.1					
0.12					
0.38					
1.4					
0.05					
0.33					
0.7					
13					
3.8					
1.4					
465					
3.5					

TABLE 2: EXPOSURE EQUATIONS AND PARAMETER DISTRIBUTIONS FOR THE FARM FAMILY RECEPTOR

Parameter	*Symbol*	*Distribution*	*Point Estimate or Custom*	*Mean*	*Most Likely*	*Standard Deviation*	*Minimum*	*Maximum*	*Probability/ Value*	*Reference*
Ingestion rate of milk (L d^{-1}) - *Child*	$U_{milk(c)}$	Lognormal	---	0.67	---	0.968	---	---	---	USDA, 1955; 1966; 1978
Bioavailability of mercury following ingestion of food (unitless)	$B_{oral\,food}$	Point	1.0	---	---	---	---	---	---	Prof. judgement
Fraction of milk consumed that was home-produced (unitless)	f_{mh}	Triangular	---	0.68	1.0	---	0.04	1.0	---	USDA, 1955; 1966; 1978
Surface water → Livestock → Beef → Humans [Adult (a) and Child(c)]	$Dose_{water\text{-}beef} = (C_{water} \times Q_{water(b)} \times f_{wbc} \times F_{f(w)} \times U_{beef(a\ or\ c)} \times B_{oral\text{-}food} \times f_{bh}) \,/\, BW_{(a\ or\ c)}$									
Ingestion of surface water by beef cattle (L d^{-1})	$Q_{water(b)}$	Cumulative	---	---	---	---	---	---	0.33, 0.33, 0.33 / 38, 45, 50	McKone, 1988
Fraction of water ingested by beef cattle that was from East Fork Poplar Creek (unitless)	f_{wbc}	Point	1.0	---	---	---	---	---	---	Prof. judgement
Biotransfer factor from cattle intake (water) to beef (mg L^{-1})/(mg d^{-1})	$F_{f(w)}$	Log-triangular	---	---	0.001	---	0.0001	0.01	---	Vreman et al., 1986
Ingestion rate of beef (kg d^{-1}) - *Adult*	$U_{beef(a)}$	Lognormal	---	0.12	---	0.186	---	---	---	USDA, 1955; 1966; 1978
Ingestion rate of beef (kg d^{-1}) - *Child*	$U_{beef(c)}$	Custom	Adult beef ingestion rate (kg d^{-1}) × Child body weight (kg) / 70 kg						---	USDA, 1955; 1966; 1978
Bioavailability of mercury following ingestion of food (unitless)	$B_{ing\text{-}food}$	Point	1.0	---	---	---	---	---	---	Prof. judgement
Fraction of beef consumed that was home-produced (unitless)	f_{bh}	Triangular	---	0.67	1.0	---	0	1.0	---	USDA, 1955; 1966; 1978
Fish → Humans (Ingestion) [Adult (a) and Child (c)]	$Dose_{fish} = (C_{fish} \times U_{fish(a\ or\ c)} \times B_{oral\text{-}food} \times f_{fc(a\ or\ c)}) \,/\, BW_{(a\ or\ c)}$									
Ingestion rate of fish from East Fork Poplar Creek (kg d^{-1}) - *Adult*	$U_{fish(a)}$	Lognormal	---	0.0012	---	2.9	---	---	---	Ebert, 1996

ChemRisk/Shonka Research Associates, Inc., Document Request Form

(This section to be completed by subcontractor requesting document)

J. Lamb / K-25 ER
Requestor / Document Center (is requested to provide the following document)

Date of request 10/23/96 Expected receipt of document 11/23/96

Document number ORNL/M-2373 Date of document 6/9/83

Title and author (if document is unnumbered)

(This section to be completed by Document Center)

Date request received 10/28/96

Date submitted to ADC NA

Date submitted to HSA Coordinator 10/28/96

(This section to be completed by HSA Coordinator)

Date submitted to CICO NA

Date received from CICO Previously Released 9/21/92

Date submitted to ChemRisk/Shonka and DOE 10-30-96

(This section to be completed by ChemRisk/Shonka Research Associates, Inc.)

Date document received

Signature

COPY Mercury 008616

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
POST OFFICE BOX X
OAK RIDGE, TENNESSEE 37830

June 9, 1983 ORNL/M-2373

Mr. J. F. Wing, Chief
Environmental Protection Branch
Department of Energy
Oak Ridge Operations
Post Office Box E
Oak Ridge, Tennessee 37830

ALL ONSITE: soil, sed, bldg

Dear Mr. Wing:

MERCURY IN SOIL AND SEDIMENT AT ORNL

As requested by G. Marciante of your staff, we are enclosing three sets of sediment and soil data: White Oak Creek Sediment (1979 samples), White Oak Creek Sediment (1983), and soil core samples adjacent Buildings 3503 and 3592. Maps showing the sample points for each group are also enclosed. The points for the 1983 White Oak Creek sediment samples are shown on two map segments. Assessment of the environmental impact of this data is underway, and methyl mercury analysis is being performed on several of the higher samples.

Also enclosed are the results of the mercury sampling performed by the Industrial Hygiene Department in Buildings 4501, 3503, and 3592.

Sincerely,

T. W. Oakes

T. W. Oakes
ORNL Environmental Coordinator
Industrial Safety and Applied
Health Physics Division

TWO:WFO:aw

Attachments

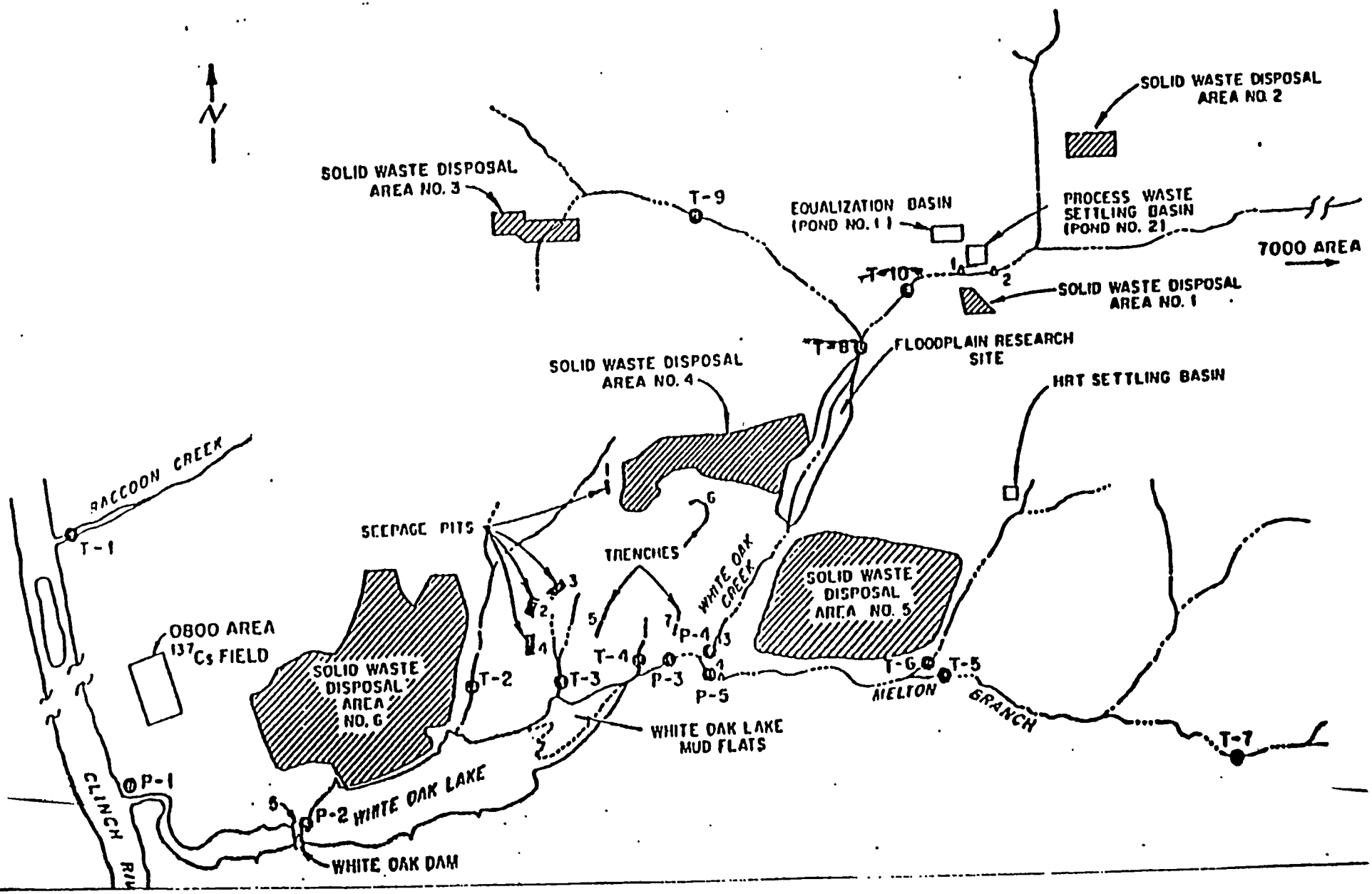
xc: R. L. Egli, DOE
D. E. Ferguson
A. S. Garrett
D. C. Parzyck

1979 Mercury in Sediment* of White Oak Creek
(ppm dry weight)

Sample Point	Concentration
P-1	0.11
P-2	3.3
P-3	2.2
P-4	2.3
P-5	0.03
~~P-6~~	~~[illegible]~~
T-1	0.05
T-2	0.06
T-3	0.04
T-4	0.04
T-5	0.02
T-6	0.04
T-7	0.02
~~T-8~~	~~[illegible]~~
T-9	0.04
~~T-10~~	~~[illegible]~~

* Surface sediment (<3 inches deep)

ORNL-DWG



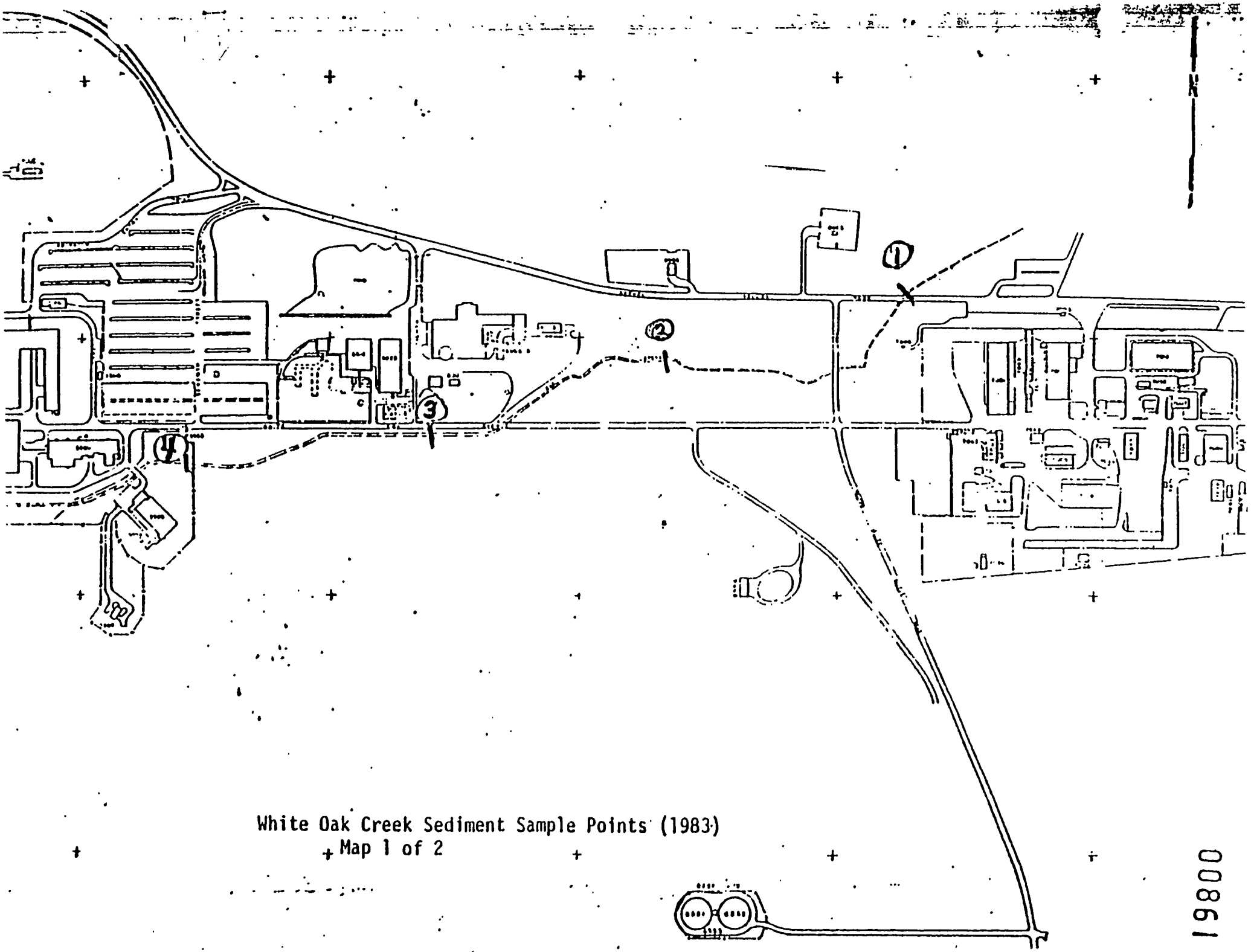
1979 Sediment Sample Points

Mercury Sample Results for Sediment in White Oak Creek (1983)

Sample Location	Core Segment	Mercury (ppm dry weight)
1-R(1)	C(2)	0.1
3-R	C	0.2
4-L	C	0.2
5-M	T	0.3
5-M	M	0.2
5-M	B	0.2
5-L	T	0.2
5-L	M	0.2
5-L	B	0.1
6-L	T	2.9
6-L	M	2.0
6-L	B	6.4
6-R	T	9.5
6-R	M	1.6
6-R	B	2.8
7-R	T	5.1
7-R	M	18
7-R	B	19
7-L	T	8.1
7-L	B	0.4
8-R	T	2.5
8-R	M	4.5
8-R	B	1.4
9-R	C	0.1
9-L	C	6.7

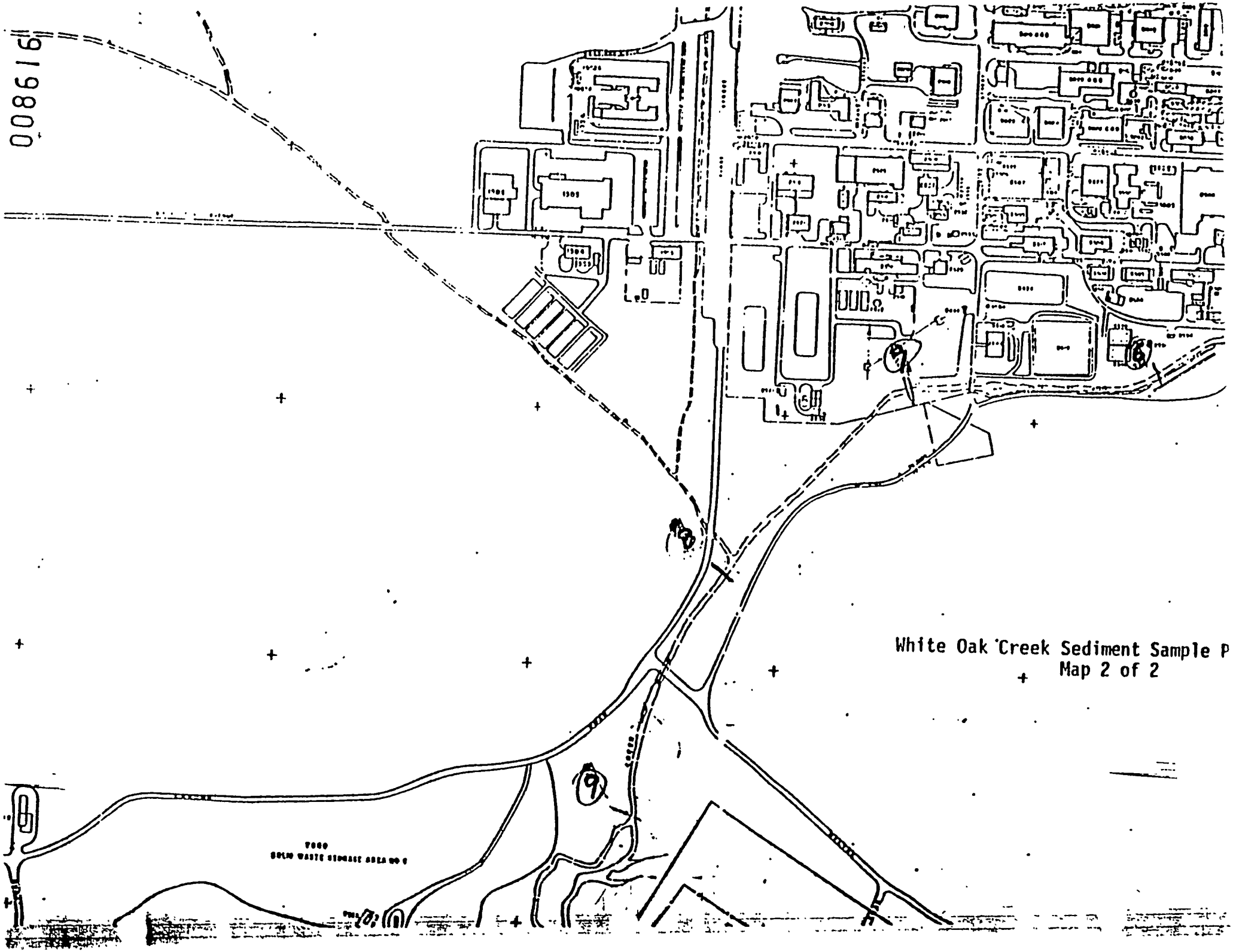
1. R, M, and L indicate the right, middle, and left of the stream looking downstream

2. T, M, B, and C indicate the top, middle, bottom, and composite of a 10-inch core



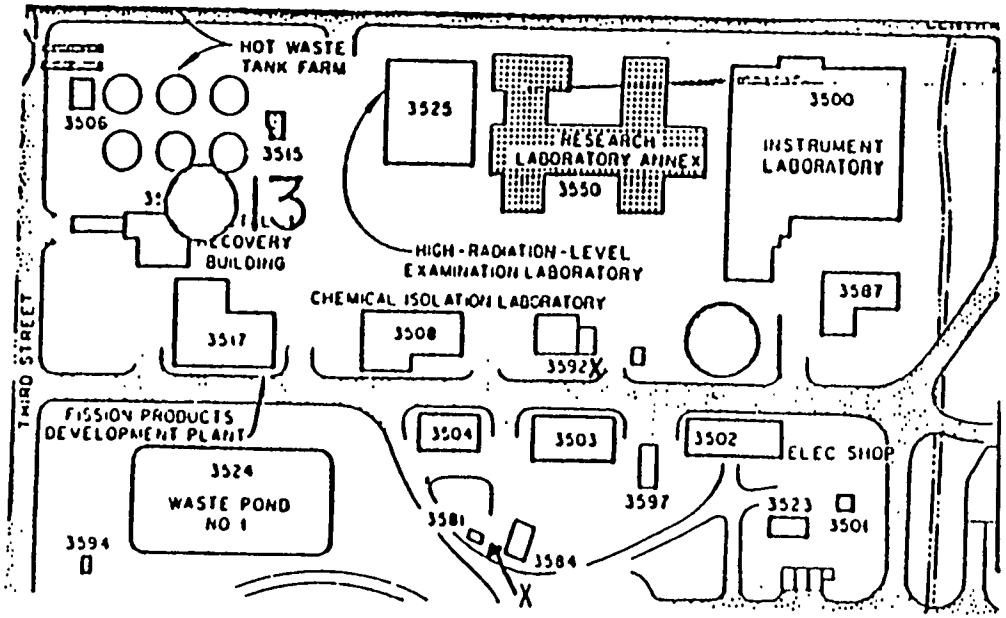
White Oak Creek Sediment Sample Points (1983)
Map 1 of 2

19800


White Oak Creek Sediment Sample P
Map 2 of 2

Mercury Results for Soil Samples Taken Near Buildings (ppm dry weight)

Sample Location	Concentration
South of Bldg. 3503	
Storage Area 1	25
Storage Area 2	3.2
Storage Area 3	6.5
Storage Area 4	0.8
Building 3592	
Sample 1	4.1
Sample 2	8.8
Sample 3	320



X Soil Sample Locations

INTRA-LABORATORY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY

June 9, 1983

To: K. W. Sommerfeld

From: A. S. Garrett, Jr., M.D. (4-7431)

Subject: Industrial Hygiene Sampling for Mercury

Attached you will find several examples of mercury sampling by the Industrial Hygiene Dept. in recent days at the three sites that we are aware that there have been mercury projects in the past, i.e., Bldgs. 4501, 3503 and 3592. Two different sampling techniques have been used. One is a TLV immediate read-out instrument that has a detection limit for mercury of .005 mg/m^3. Of those measurements done by this technique, you will notice that almost all of them are reported as less than .005 mg/m^3, meaning that it was below the detection capability of this piece of equipment. There was one sample in Bldg. 3592 where the sample was taken directly in a floor drain. The result was .01 mg/m^3. This compares with the Threshold Limit Value allowable exposure on a time weighted average of .05 mg/m^3 allowed, so even in the floor drain the air level was only about 20 percent of that allowed.

The other technique of sampling involves long-term collection on activated charcoal and analyzed by atomic absorption methods. By this technique the threshold of detection is .001 mg/m^3. You will note that samples are reported as less than .001, with the exception of the sample done on 5-26-83 in 4501, that is reported as .002 mg/m^3, and another sample done on 5-25 in Bldg. 4501 that also was reported as .002.

All of this amounts to the fact that so far in our sampling program, we have found no areas where there is airborne mercury that comes anywhere near allowable limits for exposure. We plan to do some additional monitoring and will give you a follow-up report of the results.

ASG:ph

Attachment

Air Sampling for Mercury Vapor

(Long-term samples collected on activated charcoal and analyzed by AA method)

Date	Bldg/Location	Sample Duration (Minutes)	Air Concentration (mg/m^3)
5/26/83	4501, directly over sump #2	373	< 0.001
"	4501, GB-74, SW	380	0.002
"	3503, SW Corner	405	< 0.001

Air Sampling for Mercury Vapor

Building 4501

Date	Location	Air Concentration (mg/m^3)
6/6/83	First Level	
	* Rm. 102 (Three locations)	< 0.005
	* Rm. 105 (Three locations)	"
	* Rm. 106 - Drain	"
	* Rm. 106 (Three locations)	"
	* Rm. 108 - Drain	"
	* Rm. 108 (Three locations)	"
	* Rm. 110 - Drain	"
	* Rm. 110 (Three locations)	"
	* Rm. 111 (Three locations)	"
	* Rm. 116 (Three locations)	"
	* Rm. 117A (Three locations)	"
	* Rm. 118 (Three locations)	"
	* Rm. 119 (Three locations)	"
	* Rm. 120 (Three locations)	"
	* Rm. 122 - Drain	"
	* Rm. 122 (Three locations)	"
	* Rm. 123 - Drain	"
	* Rm. 123 (Three locations)	"
	* Rm. 127 - Outside in Hall	"
	* Machine Shop (Three locations)	"
	* East East-West Hall	"
	* West East-West Hall	"
6/6/83	Second Level	
	* Rm. 201 (Three locations)	< 0.005
	* Rm. 206 (Three locations)	"
	* Rm. 208 - Drain	"
	* Rm. 208 (Three locations)	"
	* Rm. 210 - Drain	"
	* Rm. 210 (Three locations)	"
	* Rm. 212 - Drain	"
	* Rm. 212 (Three locations)	"
	* Rm. 220 (Six locations)	"
	* Rm. 221 (Three locations)	"
	* Locker Room (Three locations)	"
6/6/83	Basement	
	* Sump in BG 74	< 0.005

Building 4501, Cont'd

Date	Location	Air Concentration (mg/m^3)
6/6/83	Basement	
	* Sump West of BG 74	< 0.005
	* Sump No. 1	"
	* Large Sump East 4501	"
	* Large Sump NW 4500N	"
	* Center of Basement	"
	* East Basement	"
	* West Basement	"
	* Center BG 74	"

* Represent many single readings - grab samples taken with direct-reading mercury vapor analyzer.

Air Sampling for Mercury Vapor

Building 3592

Date	Location	Air Concentration (mg/m^3)
6/6/83	* First Floor - Center of Room	< 0.005
	SW Corner	"
	SE Corner	"
	NW Corner	"
	NE Corner	"
	Floor Drain	0.01
	* Second Floor - Center of Room	< 0.005
	SW Corner	"
	SE Corner	"
	NW Corner	"
	NE Corner	"
	Floor Drain	"
	* Outside Building - N Side	< 0.005
	E Side	"
	S Side	"
	W Side	"
	Between Bldg. 3592 & 3541	"

Building 3503

Date	Location	Air Concentration (mg/m^3)
6/6/83	* West End of Building	
	First Floor - SW Corner	< 0.005
	Center of Room	"
	N. Side of Room	"
	S. Side of Room	"
	E. Side of Room	"
	Second Floor - Catwalk	"
	* East End of Building	< 0.005
	First Floor - Center of Room	"
	N. Side of Room	"
	S. Side of Room	"
	E. Side of Room	"
	W. Side of Room	"

Building 3503, Cont'd.

Date	Location	Air Concentration (mg/m^3)
6/6/83	* Second Floor - East Side	< 0.005
	S. Side Catwalk	"
	N. Side Catwalk	"
	W. Side Catwalk	"
	Offices	"
	Labs	"
	* Change Room	< 0.005
5/27/83	* W. End of Building	< 0.005
	SW Corner	"

* Represent many single reading - grab samples taken with direct-reading mercury vapor analyzer.

008616

INTRA-LABORATORY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY

June 1, 1983

To: A. S. Garrett, Jr.

From: J. A. Ealy (4-6167) JAE/JH

Subject: Industrial Hygiene Survey

The results of the industrial hygiene samples recently conducted in your area have been determined. The results of the samples do not exceed the TLV*. This means that at the time the sampling was conducted, the operation was considered safe. Further sampling may be required if the operation is changed in any way or to verify these or any previous results.

Thank you for your cooperation in this matter. If you have any questions please contact our department.

Area Air Sampling Results

Date	Contaminant	TLV*	Concentration	Location
5/25/83	Mercury	0.05 mg/m^3	< 0.001 mg/m^3	Bldg. 3503
"	Mercury	"	< 0.001 mg/m^3	"

Comments or Recommendations:

*The Threshold Limit Value (TLV) is based on a time-weighted average (TWA) concentration for a normal 8-hour workday or 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects.

cc: WEP (Bldg. File)

INTRA-LABORATORY CORRESPONDENCE

OAK RIDGE NATIONAL LABORATORY

001

June 1, 1983

To: A. S. Garrett, Jr.

From: J. A. Ealy (4-6167)

Subject: Industrial Hygiene Survey

The results of the industrial hygiene samples recently conducted in your area have been determined. The results of the samples do not exceed the TLV*. This means that at the time the sampling was conducted, the operation was considered safe. Further sampling may be required if the operation is changed in any way or to verify these or any previous results operation is changed in any way or to verify these or any previous results

Thank you for your cooperation in this matter. If you have any quest please contact our department.

Area Air Sampling Results

Date	Contaminant	TLV*	Concentration	Location
5/25/83	Mercury	0.05 mg/m^3	< 0.001 mg/m^3	Bldg. 4501
"	Mercury	"	< 0.001 mg/m^3	"
"	Mercury	"	< 0.001 mg/m^3	"
"	Mercury	"	0.002 mg/m^3	"

Comments or Recommendations:

*The Threshold Limit Value (TLV) is based on a time-weighted average (TWA) concentration for a normal 8-hour workday or 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adver effects.

cc: WEP (Bldg. File)